Allylation of arenes catalysed by thiolate-bridged diruthenium complexes

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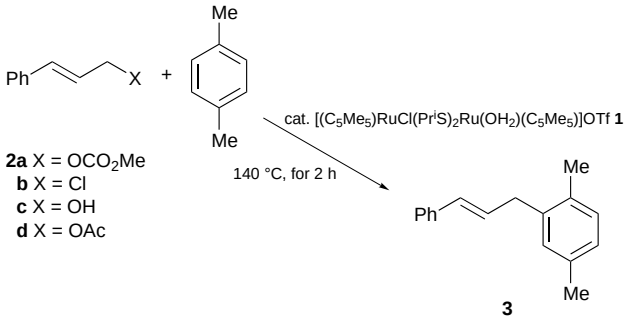
In the presence of catalytic amounts of cationic thiolate-bridged diruthenium complexes, arenes react with allylic alcohols to afford the corresponding allylated aromatic products in high yields.

Novel functions of multinuclear complexes in homogeneous catalysis are of current interest because such complexes can be expected to provide new types of reactive sites.[1] We have investigated the synthesis and reactivities of thiolate- or sulfur-bridged multinuclear complexes,[2–7] and have disclosed that a series of thiolate-bridged diruthenium complexes promote unique transformations of various substrates including acetylenes,[3] alkyl halides,[4] hydrazines,[5] aromatic aldehydes[6] and alkenes.[7] Attention has now been focused on the reactivity of allylic compounds at the diruthenium core. Although allylation of nucleophiles or electrophiles with allylic compounds has been extensively studied using various mononuclear transition metal complexes,[8] reactions of allylic compounds with arenes are still limited to the nickel- and palladium-catalysed allylation with arylmagnesium halides.[9] We envisaged the allylation of arenes with allylic compounds catalysed by thiolate-bridged diruthenium complexes, and preliminary results are reported herein.

Treatment of cinnamyl methyl carbonate **2a** with *p*-xylene in the presence of a catalytic amount of the cationic thiolate-bridged diruthenium complex $[(C_5Me_5)RuCl(SPr^i)_2Ru(OH_2)(C_5Me_5)]$ **1** at 140 °C for 2 h under nitrogen afforded (*E*)-2-cinnamyl-1,4-dimethylbenzene **3** in 75% GLC yield (Scheme 1; Table 1, run 1). A longer reaction time (6 h) improved the yield of **3** (run 2). However, no reaction occurred using other thiolate-bridged diruthenium complexes such as $[(C_5Me_5)RuCl(SPr^i)]_2$, $[(C_5Me_5)Ru(SPr^i)_2Ru(C_5Me_5)]$ and $[(C_5Me_5)Ru(SPr^i)_3Ru(C_5Me_5)]$. Furthermore, $[(C_5Me_5)RuCl_2]_2$, which reacts smoothly with **2a** to afford a mononuclear (η^3-allyl)ruthenium complex,[10] showed only low catalytic activity. When cinnamyl chloride **2b** or *trans*-cinnamyl alcohol **2c** was used instead of **2a**, **3** was obtained in almost quantitative yield (runs 3, 4 and 6). On the other hand, cinnamyl acetate **2d** was less reactive than cinnamyl alcohol **2c** (run 8).



Scheme 1

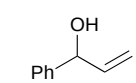
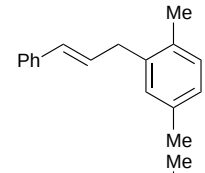
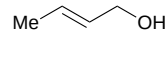
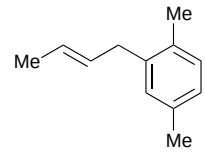
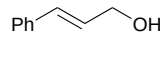
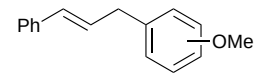
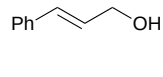
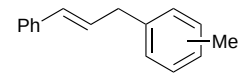
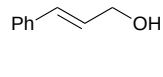
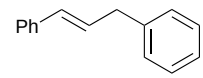
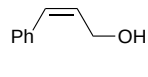
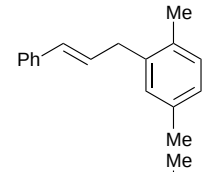
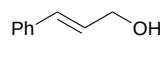
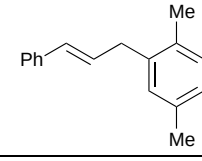
Table 1 Ruthenium-catalysed allylation of *p*-xylene with cinnamyl compounds[a]

Run	**1**/mol%	Substrate	Yield of **3** (%)[b]
1	5	**2a**	75
2[c]	5	**2a**	> 99
3	5	**2b**	> 99
4	1	**2b**	> 99
5	0.2	**2b**	60
6	5	**2c**	> 99
7	1	**2c**	30
8	5	**2d**	17

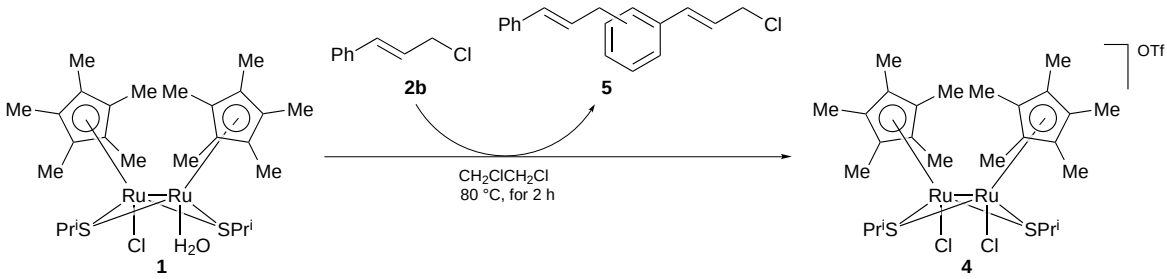
[a] All the reactions were carried out with a cinnamyl compound (0.25 mmol) and *p*-xylene (10 ml) at 140 °C for 2 h. [b] GLC yield. [c] For 6 h.

Recently, catalytic reactions that do not use organic halides have been receiving much attention because the production of unnecessary halogen-containing byproducts is avoided. Thus

Table 2 Ruthenium-catalysed allylation of aromatic compounds[a]

Run	Allylic compound	Aromatic compound	Product	Yield (%)[b]
1		*p*-Xylene		> 99[c]
2[d]		*p*-Xylene		64
3		Anisole		59[e]
4[f]		Toluene		52[g]
5[h]		Benzene		27
6		*p*-Xylene		11[c]
7[i]		*p*-Xylene		> 99[c]

[a] All the reactions were carried out in the presence of **1** (5 mol%) with an allylic compound (0.50 mmol) and an aromatic compound (20 ml) at 140 °C for 2 h. [b] Isolated yield. [c] GLC yield. [d] For 5 h. [e] Isomer ratio was *o*:*m*:*p* = 12:0:88. [f] At 110 °C. [g] Isomer ratio was *o*:*m*:*p* = 0:65:35. [h] At 80 °C. [i] **4** was used instead of **1**.



Scheme 2

the reactivities of allylic alcohols have been investigated in detail. The allylation of *p*-xylene, anisole, toluene and benzene with allylic alcohols afforded the corresponding allylic aromatic compounds in good yields. Typical results are given in Table 2. It is noteworthy that both 1-phenylprop-2-en-1-ol and **2c** react with *p*-xylene to give the same product, **3**. This suggests that a common (π-allyl)diruthenium complex is formed as an intermediate. The reactions of anisole and toluene with cinnamyl alcohol produced a 12 : 0 : 88 (*o* : *m* : *p*) mixture of (*E*)-cinnamylmethoxylbenzenes in 59% total yield (run 3) and a 0 : 65 : 35 (*o* : *m* : *p*) mixture of (*E*)-cinnamylmethyl benzenes in 52% total yield (run 4). Interestingly, the reaction between *cis*-cinnamyl alcohol and *p*-xylene proceeded very slowly at 140 °C resulting in the formation of **3** in poor yield. This is in sharp contrast to the reaction of *trans*-cinnamyl alcohol **2c** (*vide supra*).

Treatment of **1** with 5 equiv. of cinnamyl chloride **2b** in 1,2-dichloroethane at 80 °C for 2 h gave the cationic dinuclear ruthenium complex $[(C_5Me_5)Ru(SPr^i)Cl]_2[OTf]$ **4** in 29% yield, together with an allylated cinnamyl chloride **5** (Scheme 2). The structure of the paramagnetic complex **4** has been fully characterized by X-ray crystallography.† Complex **4** can also be used as a catalyst for the allylation of arenes with allylic alcohols (Table 2, run 7).

As described above, toluene was mainly allylated at the 3- and 4-positions (Table 2, run 4). This suggests that the reaction does not proceed *via* classical electrophilic aromatic substitution. Although the reaction mechanism is not yet clear, we assume that the first step involves the formation of a (π-allyl)diruthenium complex, which is followed by attack of arenes on the π-allyl moiety. In connection with this, the stereochemistry of the allyl moiety in allylated products was completely controlled, in contrast to the Lewis acid-catalysed allylation reactions of aromatic compounds.[11] This allylation of arenes with allylic alcohols using diruthenium complexes provides a new methodology for carbon–carbon bond formation. Molybdenum- and tungsten-catalysed allylation of aromatic compounds has very recently been reported, however, the catalytic activities of thiolate-bridged diruthenium complexes are much better than those of molybdenum and tungsten complexes.[12] Further studies on the detailed reaction mechanism and the application to organic synthesis are now in progress.

Footnote

† Detailed experimental results will be reported in due course.

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