

# Ruthenium Complexes Containing Diamine-Based Ligands as Catalysts for Insertion of Carbenes into O-H Bonds of Alcohols

François Simal, Albert Demonceau,\* and Alfred F. Noels

*Laboratory of Macromolecular Chemistry and Organic Catalysis, C.E.R.M.  
University of Liège, Sart-Tilman (B.6a), B-4000 Liège, Belgium*

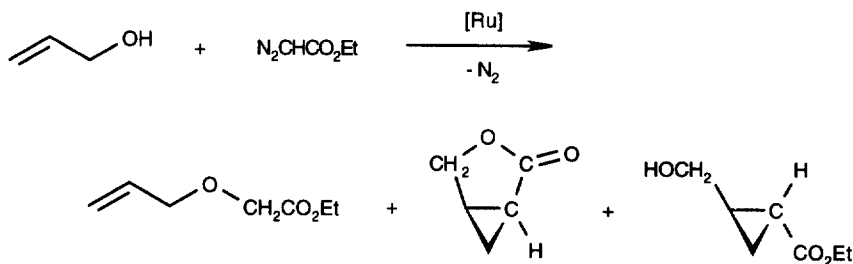
Received 2 September 1998; accepted 3 November 1998

## Abstract

Ruthenium complexes with *N*-(*p*-toluenesulfonyl)-diamine ligands are efficient catalysts for insertion of carbenes generated from diazo compounds into O-H bonds of alcohols. © 1998 Elsevier Science Ltd. All rights reserved.

*Keywords:* Insertion reactions; Alcohols; Diazo compounds; Ruthenium and compounds.

Dirhodium(II) tetracarboxylate-catalysed insertions of carbenes into aliphatic C-H [1] and polar X-H bonds [2] have been used increasingly for the synthesis of carbo- and heterocycles [3, 4]. To our knowledge, despite ruthenium is a cheap metal, and many of its complexes readily available, easily chemically engineered, and being increasingly popular in cyclopropanation reactions [5, 6], they only have scarcely been investigated to date in insertion reactions [5e, 7]. We recently explored the synthesis of various ruthenium complexes with *N*-(*p*-toluenesulfonyl)-diamine ligands, and used them as catalysts or catalyst precursors for olefin cyclopropanation [8]. As a continuation of this research we became interested in the addition of diazo compounds to olefinic alcohols in order to assess the chemoselectivity between O-H insertion and cycloaddition to the C-C double bond. In this investigation, allyl alcohol was chosen as the model substrate [9].



Fax : ++32-4-366 34 97. E-mail : A.Demonceau@ulg.ac.be

The following chelate complexes with bidentate TsN-N ligands have been synthesized [10] and tested in this investigation, and we found that O-H insertion was highly selective to the detriment of olefin cyclopropanation (Table 1). Such chemoselectivity is reminiscent of that observed

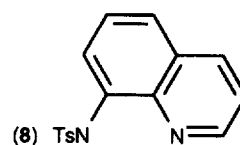
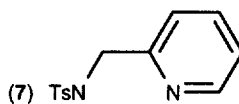
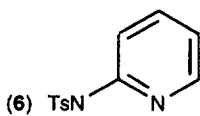
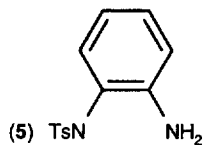
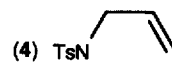
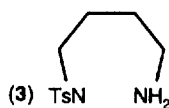
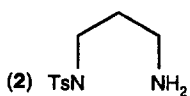
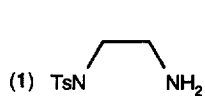
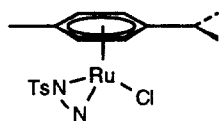


Table 1

Addition of ethyl diazoacetate to allyl alcohol in the presence of ruthenium complexes 1-8<sup>a</sup>

Catalyst (TGA)	Yield, % <sup>b</sup>		Catalyst (TGA)	Yield, % <sup>b</sup>	
	O-H Insertion	Cyclopropanation		O-H Insertion	Cyclopropanation
1 (221 °C)	80	7.5	5 (211 °C)	80	10
2 (-c)	75	6	6 (269 °C)	56	7
3 (-c)	57	4	7 (210 °C)	83	4
4 (185 °C <sup>c</sup> )	82	6.5	8 (271 °C)	15	2

<sup>a</sup> Reaction conditions : catalyst, 0.005 mmol; allyl alcohol, 20 mmol; ethyl diazoacetate, 1 mmol diluted by the substrate up to 1 mL; addition time, 4 h; temperature, 60 °C.

<sup>b</sup> Based on ethyl diazoacetate and determined by GLC analysis.

<sup>c</sup> A side decomposition of the complex is competitive with arene release.

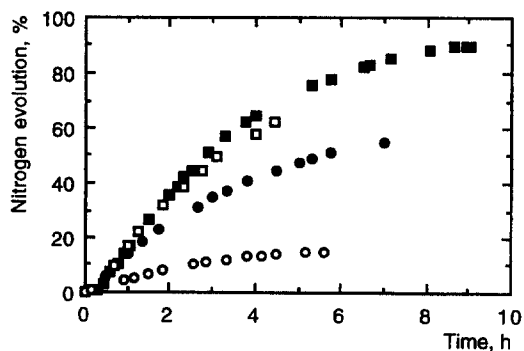


Figure 1

Influence of the ligands on the decomposition rate of ethyl diazoacetate in allyl alcohol in the presence of complexes 1 (■), 2 (□), 3 (●), and 8 (○), at 60 °C.

Reaction conditions same as in Table 1.

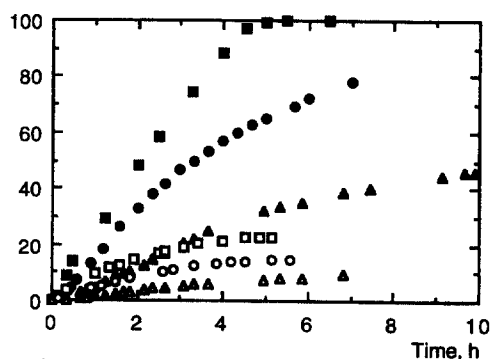


Figure 2

Influence of the temperature on the decomposition rate of ethyl diazoacetate in allyl alcohol in the presence of complexes 7 (■, ●, ▲) and 8 (□, ○, △), at 40 °C (▲, △), 60 °C (●, ○) and 80 °C (■, □).

Reaction conditions same as in Table 2.

Table 2  
Effect of the temperature on the yield of the addition of ethyl diazoacetate to allyl alcohol<sup>a</sup>

Catalyst	O-H Insertion yield (cyclopropanation yield), % <sup>b</sup>			
	Temperature : 40 °C	60 °C	80 °C	Reflux, 96 °C
1	27 (2)	80 (7.5)	83 (10.5) <sup>c</sup>	80 (11)
7	37 (1)	83 (4)	88 (5.5)	79 (7)
8	7 (<1)	15 (2)	31 (5)	43 (7)

<sup>a,b</sup> Reaction conditions same as in Table 1.

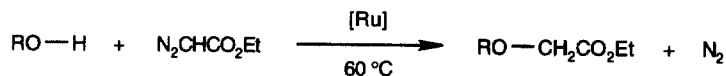
<sup>c</sup> Catalyst 3 : O-H insertion yield, 85 %; cyclopropanation yield, 8 %.

with rhodium carboxylates [9].

The steric and electronic properties of the ligands have a dramatic influence on the reactivity of the ruthenium catalysts. The importance of the bite angle (the angle between the two donor atoms of the bidentate ligand and the metal centre) is illustrated by comparing the activity of complexes 1, 2, and 3 (Table 1 and Figure 1). Distortions of this angle mostly affected the decomposition rate of the diazo compound and hence the overall yield of the reaction, but not significantly the chemoselectivity. In the series of complexes 1, 2 and 3, the former was shown to be more efficient than the latter. Ligands combining both a tosylanilide and a pyridine (or a quinoline) moiety, 6 and 8, gave rise to less efficient catalytic systems (whatever the bite angle of the resulting chelate complex) than tosylamide-amine (1-3), tosylanilide-aniline (5), and tosylamide-pyridine (7) derivatives.

Complexes 1-8 are 18-electron species and, in order to display some catalytic activity, (at least) one ligand should be displaced by the diazo compound. According to the literature [11], the resulting metal-diazo compound complex should then lose one nitrogen molecule and afford a ruthenium-carbene intermediate. In this context, the allyl group of chelate 4 is an obvious candidate for ligand displacement. With the other complexes, the amine, aniline or pyridine moieties could be displaced despite their good coordination ability and the entropy effect. Most likely is the release of the *p*-cymene ligand, as it was shown for RuCl<sub>2</sub>(*p*-cymene)(PR<sub>3</sub>)-catalysed olefin metathesis [12]. Furthermore, the close parallelism observed between the ease with which the arene ligand is disengaged from the different RuCl(*p*-cymene)(TsN-N) complexes reported in Table 1 (as quantified by standardised thermogravimetric analyses (TGA)) indicates a direct relationship between arene ligand lability and catalyst activity. This is clearly illustrated by complexes 6 and 8 whose temperature of release of the *p*-cymene ligand (270 °C) is much higher than that of the other complexes used in this study (Table 1).

Whatever the actual activation process of these complexes, the most active ones proved to efficiently promote carbene insertion into the O-H bond of a variety of substrates. The yields ranged from 75 to 95 % provided the temperature be higher than 50 °C (Table 2).



R = H, Me, Et, Pr, *i*-Pr, *n*-Bu, *sec*-Bu, *t*-Bu, Ph, Bn, and Ac.

Primary alcohols were more reactive than tertiary ones, as confirmed by intermolecular competitions (Table 3). The reason why sterically hindered alcohols such as *t*-butanol were less reactive likely arises from the lower accessibility of the oxygen lone pairs to the electrophilic ruthenium-carbene intermediate.

Table 3  
Relative reactivities of representative alcohols and styrene<sup>a,b</sup>

Substrate	Catalyst	
	RuCl( <i>p</i> -cymene)(N-N-1)	RuCl( <i>p</i> -cymene)(N-N-7)
Methanol	1.04	1.12
Ethanol	1.00	1.00
Propanol	0.97	0.97
Isopropanol	0.63	0.67
<i>t</i> -Butanol	0.24	0.32
Allyl alcohol <sup>c</sup>	0.91	0.89
Styrene <sup>d</sup>	0.62	0.96

<sup>a,b</sup> Reaction conditions same as in Table 1 (60 °C).

<sup>c</sup> 0.94 with complex 6.

<sup>d</sup> With complexes 1 and 7, *cis/trans* = 0.51 and 0.53, respectively.

In conclusion new highly efficient catalysts for insertion of carbenes into O-H bonds have been developed, which display a quite good chemoselectivity towards insertion versus C-C double bond cycloaddition. Preliminary experiments also showed that the best ruthenium complexes catalysed N-H insertion of carbenes into aniline with excellent yields (85-95 %). These results will be reported in due time.

#### References

- [1] (a) Demonceau A, Noels AF, Hubert AJ, Teyssié P. *J. Chem. Soc., Chem. Commun.* 1981:688-689. (b) Demonceau A, Noels AF, Hubert AJ, Teyssié P. *Bull. Soc. Chim. Belg.* 1984;93:945-948. (c) Demonceau A, Noels AF, Hubert AJ. *J. Mol. Catal.* 1989;49:L13-L17. (d) Demonceau A, Noels AF, Hubert AJ. *J. Mol. Catal.* 1989;57:149-152.
- [2] (a) Paulissen R, Reimlinger H, Hayez E, Hubert AJ, Teyssié P. *Tetrahedron Lett.* 1973;14:2233-2236. (b) Paulissen R, Hayez E, Hubert AJ, Teyssié P. *Ibid.* 1974;15:607-608.
- [3] (a) Taber DF. *Comprehensive Organic Synthesis*, Vol. 3. Pattenden G, editor. Oxford: Pergamon Press, 1991:1045. (b) Taber DF, Stiriba S-E. *Chem. Eur. J.* 1998;4:990-992.
- [4] (a) Miller DJ, Moody CJ. *Tetrahedron* 1995;51:10811-10843. (b) Aller E, Buck RT, Drysdale MJ, Ferris L, Haigh D, Moody CJ, Pearson ND, Sanghera JB. *J. Chem. Soc., Perkin Trans. I* 1996:2879-2884.
- [5] (a) Demonceau A, Noels AF, Saive E, Hubert AJ. *J. Mol. Catal.* 1992;76:123-132. (b) Demonceau A, Saive E, de Froidmont Y, Noels AF, Hubert AJ, Chizhevsky IT, Lobanova IA, Bregadze VI. *Tetrahedron Lett.* 1992;33:2009-2012. (c) Demonceau A, Abreu Dias E, Lemoine CA, Stumpf AW, Noels AF, Pietraszuk C, Gulinski J, Marciniak B. *Ibid.* 1995;36:3519-3522. (d) Demonceau A, Lemoine CA, Noels AF, Chizhevsky IT, Sorokin PV. *Ibid.* 1995;36:8419-8422. (e) Demonceau A, Simal F, Noels AF, Viñas C, Nuñez R, Teixidor F. *Ibid.* 1997;38:4079-4082.
- [6] (a) Bergbreiter DE, Morvant M, Chen B. *Tetrahedron Lett.* 1991;32:2731-2734. (b) Maas G, Werle T, Alt M, Mayer D. *Tetrahedron* 1993;49:881-888. (c) Nishiyama H, Itoh Y, Matsumoto H, Park S-B, Itoh K. *J. Am. Chem. Soc.* 1994;116:2223-2224. (d) Nishiyama H, Itoh Y, Sugawara Y, Matsumoto H, Aoki K, Itoh K. *Bull. Chem. Soc. Jpn.* 1995;68:1247-1262. (e) Park S-B, Murata K, Matsumoto H, Nishiyama H. *Tetrahedron: Asymmetry* 1995;6:2487-2494. (f) Nishiyama H, Aoki K, Itoh H, Iwamura T, Sakata N, Kurihara O, Motoyama Y. *Chem. Lett.* 1996;1071-1072. (g) Doyle MP, Peterson CS, Zhou Q-L, Nishiyama H. *J. Chem. Soc., Chem. Commun.* 1997;211-212. (h) Davies IW, Gerena L, Cai D, Larsen RD, Verhoeven TR, Reider PJ. *Tetrahedron Lett.* 1997;38:1145-1148.
- [7] Sengupta S, Das D, Sen Sarma D. *Tetrahedron Lett.* 1996;37:8815-8818.
- [8] Simal F, Demonceau A, Noels AF. *Tetrahedron Lett.* 1998;39:3493-3496.
- [9] Noels AF, Demonceau A, Petiniot N, Hubert AJ, Teyssié P. *Tetrahedron* 1982;38:2733-2739.
- [10] Haack K-J, Hashiguchi S, Fujii A, Ikariya T, Noyori R. *Angew. Chem. Int. Ed. Engl.* 1997;36:285-288.
- [11] (a) Maas G. *Top. Curr. Chem.* 1987;137:75-253. (b) Ye T, McKervey MA. *Chem. Rev.* 1994;94:1091-1160. (c) Noels AF, Demonceau A. In *Applied Homogeneous Catalysis with Organometallic Compounds*, Vol. 2, Developments; Cornils B, Herrmann WA, editors. VCH, 1996:733-747.
- [12] Demonceau A, Stumpf AW, Saive E, Noels AF. *Macromolecules* 1997;30:3127-3136.