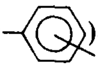
*Journal of Molecular Catalysis*, 28 (1985) 27 - 32

# TUNGSTEN PHENOXIDE CATALYSTS IN OLEFIN METATHESIS REACTIONS: RELATION BETWEEN ACTIVITY AND STEREOSELECTIVITY

F. QUIGNARD, M. LECONTE and J. M. BASSET

*Institut de Recherches sur la Catalyse, C. N. R. S., 2, avenue Albert Einstein, 69626 Villeurbanne Cédex (France)*

## Summary

Two types of tungsten phenoxide catalysts have been synthesized; *viz.* $Cl_2W(O$—  $)_4$ (A) and $Cl_4W(O$—  $)_2$ (B), respectively. When associated with $C_2H_5AlCl_2$, these precursor complexes exhibit a fair and an extremely high catalytic activity for A and B respectively. Within each series there is a relationship between activity and stereoselectivity, the most active catalysts being those which are the least stereoselective with a limiting value of unity for the *trans*/*cis* ratio of the products.

The results are explained on the basis of a simple theory which correlates the activity and the stereoselectivity with the respective energy levels of the metallacyclobutane complex and of the metallacarbene–olefin complex.

## Introduction

We have recently proposed a simple theory which accounts for the metathesis stereochemistry of any cyclic and acyclic olefin [1]. The theory is based on the relative energy levels of the various intermediate steps in the reaction pathway. In particular, the stereochemistry is governed mainly by the relative energy of the metallacyclobutane complex with respect to that of the metallacarbene–olefin complex (Fig. 1).

If the metallacarbene–olefin complex has an energy which is smaller than that of the two possible metallacyclobutanes which lead respectively to the *cis* and *trans* isomers, the resulting stereoselectivity will be governed by the energy levels of these two metallacycles. If the coordinated olefin has an energy which is higher than that of the metallacyclobutane, the stereochemistry will not be governed by the energy levels of the metallacycle and the system will lose its stereoselectivity and yield a *trans*/*cis* ratio of unity.

The parameters which may modify the respective energy levels of the intermediates are the transition metal [2], the ring strain in the cyclic *cis*- or *trans*-olefin [3], the nature of the substituents on the acyclic olefins [2, 4],

0304-5102/85/$3.30

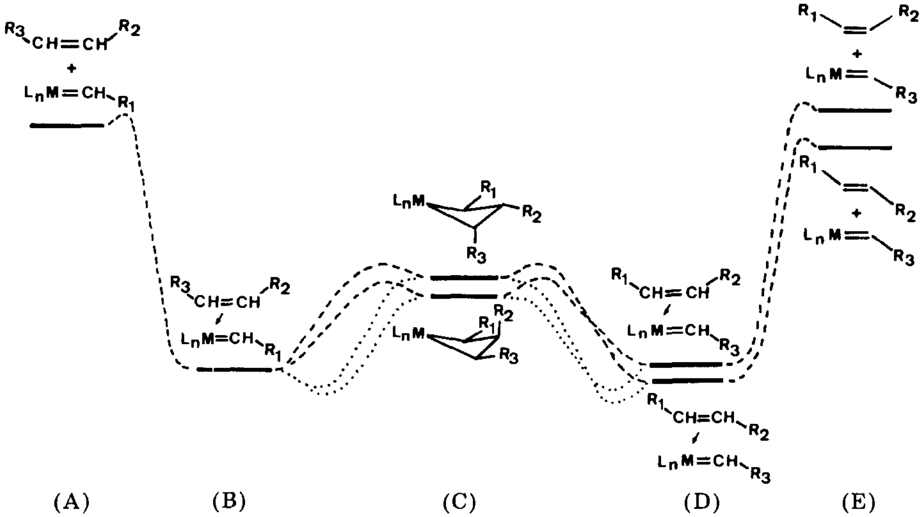
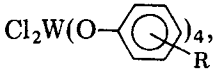
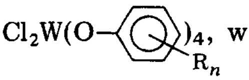
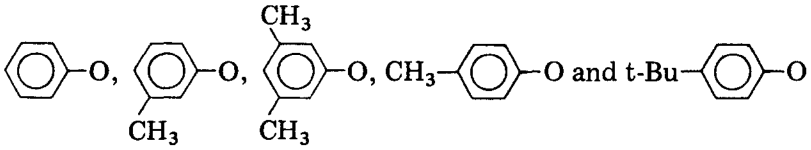


Fig. 1. Schematic energy levels for the various intermediates involved in the metathesis of an acyclic *cis*-olefin.

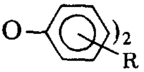
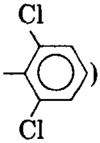
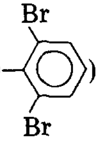
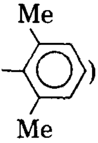
the nature of the co-catalyst (if any) and the nature of the ligands attached to the transition metal during the propagation step [5]. This last parameter is difficult to evaluate since it is impossible to know if a given ligand remains coordinated to the precursor complex during propagation. Nevertheless some recent results by Dodd *et al.* [6] with  $Cl_2W(O{-}C_6H_4R)_4$, as well as our own results using substituted phenols [7], indicate that the nature of the substituent on the ring has a profound effect on the resulting activity. It was therefore logical to check whether or not there is a relationship between the activity and the stereoselectivity with this class of catalysts; *a priori* one would expect the more active catalyst to be the less stereoselective and vice versa.

## Experimental

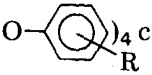
The precursor complexes  $Cl_2W(O{-}C_6H_{5-n}R_n)_4$, with the number of substituents *n* on the phenoxy ligand being 0, 1 or 2, were prepared according to the procedure described by Funk and Baumann [8], and were characterized by elemental analyses for C, H, W, Cl when the phenoxy ligands



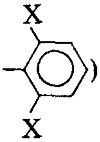
were employed.

A new class of precursor complex $Cl_4W(O$–$)_2$ was also prepared in a similar manner to those above (reaction of $WCl_6$ + 2 mol equiv of substituted phenol [9]). Elemental analyses of these materials gave the following results. Anal. calc. for $Cl_4W(O$–$)_2$: C, 22.18; H, 0.93; Cl, 43.6; W, 28.3. Found C, 22.3; H, 1.3; Cl, 42.7; W, 28.1. Anal. calc. for $Cl_4W(O$–$)_2$: C, 17.40; Br, 38.6; Cl, 17.14; W, 22.20. Found C, 17.20. Anal. calc. for $Cl_4W(O$–$)_2$: C, 32.39; H, 3.16; Cl, 25.0; W, 32.39. Found C, 31.55; H, 3.15; Cl, 24.4; W, 31.55.

## Results

All the complexes are active in *cis*-2-pentene metathesis in association with an organo-aluminium co-catalyst (Fig. 2). The stereoselectivities have been determined by plotting the *trans*/*cis* ratio of the $C_4$ olefin *versus* the *trans*/*cis* ratio for the $C_5$ olefin [2]. The extrapolated values obtained for a *trans*/*cis* ratio equal to zero for the $C_5$ olefin are given in Table 1 for the $Cl_2W(O$–$)_4$ catalysts.

From this table it will be seen that the activities vary according to the order: R = H > 3-Me > 3,5-di-Me > 4-Me > 4-t-Bu. Generally speaking, the most active catalysts are those which possess the most acidic ligands and exhibit the lowest stereoselectivities. However, even with the unsubstituted phenoxy ligand, which gives the highest activity, the corresponding stereoselectivity is far removed from unity, indicating that the metallacyclic complex has a higher energy than the metallacarbene–olefin complex (Fig. 1).

The disubstituted complexes $Cl_4W(O$–$)_2$ (X = Cl, Br) were found to be extremely active in *cis*-2-pentene metathesis (as well as α-olefins and functionalized olefins [9]). The corresponding stereoselectivity is extremely low since the *trans*/*cis* ratio for the $C_4$ olefin was 0.9, indicating an almost

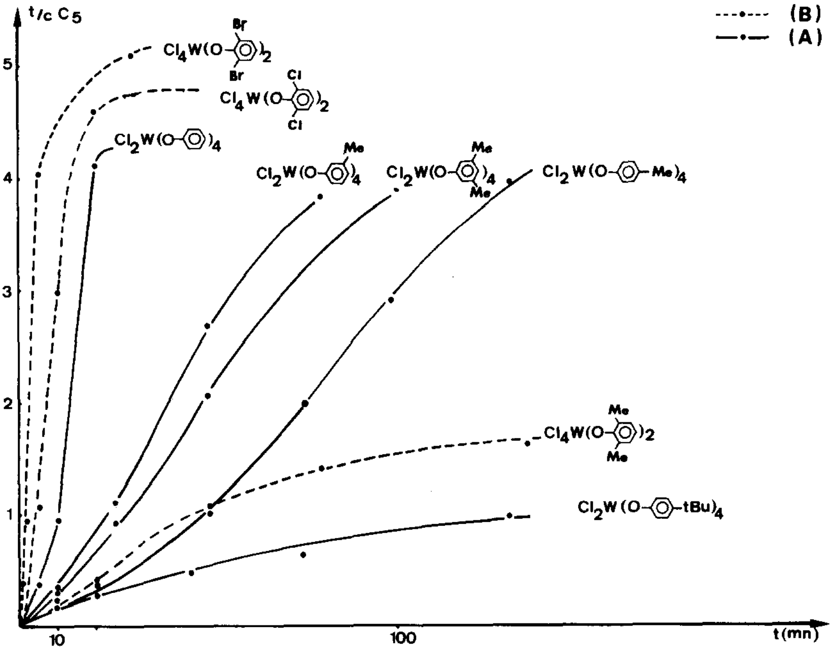
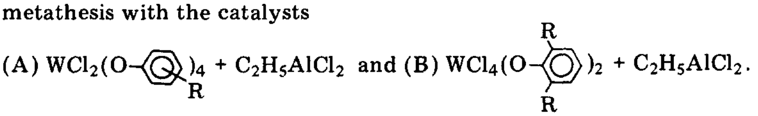


Fig. 2. Effect of substituted phenoxy ligand in the overall activity of *cis*-2-pentene metathesis with the catalysts

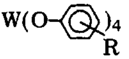


$(A)\ WCl_2(O-C_6H_4R)_4 + C_2H_5AlCl_2$ and $(B)\ WCl_4(O-C_6H_3R_2)_2 + C_2H_5AlCl_2$.

With the system (A) the following conditions were employed: solvent, chlorobenzene; co-catalyst, $C_2H_5AlCl_2$; $[W] = 1.6 \times 10^{-3}$ mol $l^{-1}$; Al/W = 6; olefin/W = 50; temperature, 25 °C. With the system (B) the following conditions were employed: solvent, chlorobenzene; co-catalyst, $C_2H_5Cl_2$; $[W] = 2.3 \times 10^{-4}$ mol $l^{-1}$; Al/W = 43; olefin/W = 360; temperature, 25 °C.

TABLE 1

Stereoselectivity of *cis*-2-pentene metathesis with the catalyst



$Cl_2W(O-C_6H_4R)_4$

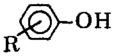
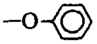
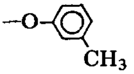
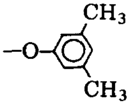
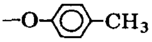
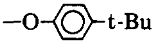
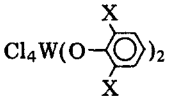
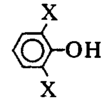
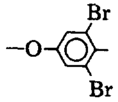
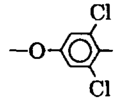
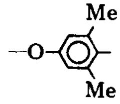
| Phenoxy ligand | p$K_a$ value of  | Activity as expressed by *trans*/*cis* ratio of $C_5$ olefin at $t$ = 30 min | Stereoselectivity as expressed by *trans*/*cis* ratio of $C_4$ olefin at 0% conversion |
|---|---|---|---|
|  | 9.99 | 4.2 | 0.76 |
|  | 10.10 | 1.4 | 0.76 |
|  | 10.20 | 1.1 | 0.74 |
|  | 10.28 | 0.65 | 0.71 |
|  | – | 0.35 | 0.70 |

TABLE 2

Stereoselectivity of *cis*-2-pentene metathesis with the catalyst  where X = Cl, Br or Me

| Phenoxy ligand | p$K_a$ value of  | Activity as expressed by *trans*/*cis* ratio of $C_5$ olefin at $t$ = 10 min | Stereoselectivity as expressed by *trans*/*cis* ratio of $C_4$ olefin at 0% conversion |
|---|---|---|---|
|  | 8.20 | 5.24 | 0.9 |
|  | 8.30 | 4.7 | 0.9 |
|  | ~10.30 | 0.21 | 0.64 |

statistical coordination of the olefin to the metallacarbene. In the same series, when X = Me the activity was found to be extremely small, and the corresponding stereoselectivity (*trans*/*cis* ratio = 0.65) was one of the smallest observed in this series (Table 2).

## Conclusions

From this preliminary work it appears that for a given series of precursor complexes and for comparable reaction conditions, there is a general rule according to which the more active catalysts are the less stereoselective and vice versa. In general, a *trans*/*cis* ratio of unity indicates an extremely active catalyst and conversely a high stereoselectivity apparently indicates poor catalytic activity. Although we have no general proof, we suggest that the stereochemistry is probably the most reliable and reproducible tool in any comparison of the activity of various catalytic systems. This observation of a relationship between activity and stereoselectivity may be deduced logically from our previous theory [1].

## Acknowledgement

We wish to thank the Société Nationale Elf-Aquitaine for supporting this work.

## References

1 C. Larroche, J. P. Laval, A. Lattes, M. Leconte, F. Quignard and J. M. Basset, *J. Org. Chem.*, *47* (1982) 2019.

2 M. Leconte and J. M. Basset, *J. Am. Chem. Soc.*, *101* (1979) 7296.

3 C. Larroche, J. P. Laval, A. Lattes, M. Leconte, F. Quignard and J. M. Basset, *J. Chem. Soc., Chem. Commun.*, (1983) 220.

4 E. A. Ofstead, J. P. Lawrence, M. L. Senyek and N. Calderon, *J. Mol. Catal.*, *8* (1980) 227.

5 M. Leconte, Y. Ben Taarit, J. L. Bilhou and J. M. Basset, *J. Mol. Catal.*, *8* (1980) 263.

6 H. T. Dodd and K. J. Rutt, *J. Mol. Catal.*, *15* (1982) 103.

7 N. Taghizadeh, F. Quignard, M. Leconte, J. M. Basset, C. Larroche, J. P. Laval and A. Lattes, *J. Mol. Catal.*, *15* (1982) 219.

8 H. Funk and W. Baumann, *Z. Anorg. Chem.*, *231* (1937) 264.

9 *Fr. Pat. 8 309 876* (1983) to J. M. Basset, M. Leconte, J. Ollivier and F. Quignard (Société Nationale Elf Aquitaine).