

## ERRATUM ( Vol 6, No. 3, 313-315, 1995)

Due to problems in the editorial process, we are reprinting, in full and with corrections, this article previously published in the *JBCS* (Vol. 6, No. 3, 313-315, 1995). Mistakenly, the disk used in the desktop publication of the article contained its original version without the suggestions made by the referees. At the time the galley-proof was correct by the authors, this mistake was not clearly noted. Thus, the article was published without all the corrections, which are now incorporated.

### A Study of a New Catalytic System for the Metathesis of Functionalized Olefins

I.M. Baibich<sup>\*a</sup>, J.R. Gregório<sup>a</sup>, C. Kern<sup>a</sup> and H. Rudler<sup>\*b</sup>

<sup>a</sup> Instituto de Química, UFRGS., Av. Bento Gonçalves 9500, Porto Alegre - RS, Brazil

<sup>b</sup> Laboratoire de Chimie Organique, URA 408, Université P. et M. Curie, T 45, 4 Place  
Jussieu, 75252 Paris Cedex 05, France

Received: June 6, 1994; March 10, 1995

Efetouou-se o estudo do novo sistema catalítico  $WCl_6.PMHS$ . Curvas de conversão, números de rotação e frequências de rotação foram comparados aos relativos aos sistemas já conhecidos na literatura. Os resultados mostram que o novo sistema tem atividades análogas nas reações de metátese do 10-undecenoato de metila e do 10-undecenonitrila análogo às dos sistemas conhecidos para esse tipo de reação, com a vantagem de utilizar como catalisador um composto menos tóxico e de menor custo que  $SnMe_4$  e  $Ph_2SiH_2$ .

The study of a new catalytic system,  $WCl_6.PMHS$  ( $PMHS$  = polymethylhydrosiloxane), was carried out. Conversion factors were compared with those for the systems  $WCl_6.SnMe_4$  and  $WCl_6.Ph_2SiH_2$ , already described in the literature. The results show that the new system has activities in the metathesis reaction of methyl-10-undecenoate and 10-undecenonitrile similar to the typical systems used for these kinds of reactions, with the advantage of using a compound which is less toxic and less expensive than  $SnMe_4$  and  $Ph_2SiH_2$  as the co-catalyst.

**Keywords:** *functionalized olefin metathesis, tungsten catalysts in metathesis, metathesis*

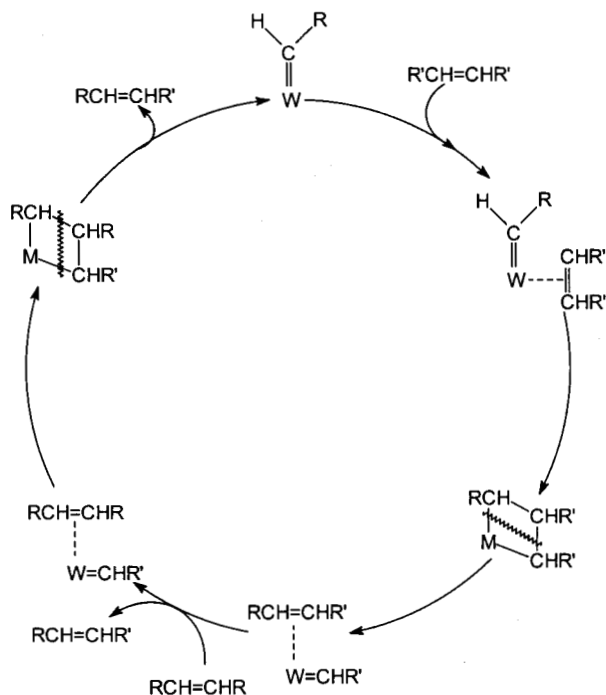
### Introduction

The field of olefin metathesis research has grown considerably, and efficient systems have been developed since the discovery of the olefin-metathesis reaction for non-functionalized olefins<sup>1,2</sup>.

This kind of reaction provides the synthesis of difunctional derivatives with well-defined structures for functionalized olefins. However, low tolerance for heteroatoms has been observed through the use of the same type of catalytic system as for non-functionalized olefins. The few systems which rendered satisfactory results were those based on the

use of  $WCl_6$  associated with either  $SnMe_4$  or  $Ph_2SiH_2$  (the so-called homogeneous systems), and also those based on  $Re_2O_7$  associated with  $SnMe_4$  on a solid support (the heterogeneous systems)<sup>3,4,5</sup>.

The recently discovered, well-defined alkylidene complexes remarkably improved the yields of the metathesis reactions of functionalized olefins<sup>6,7,8</sup>. This was also the case for the  $Al_2O_3/SiO_2$  supported  $MeReO_3$  (MTO)<sup>8</sup>. A drawback of the use of the "classical systems" is the toxicity of  $SnMe_4$ , whereas the well-defined systems are problematic because they are somewhat difficult to synthesize and/or are expensive. The mechanism involved in this type



Scheme 1.

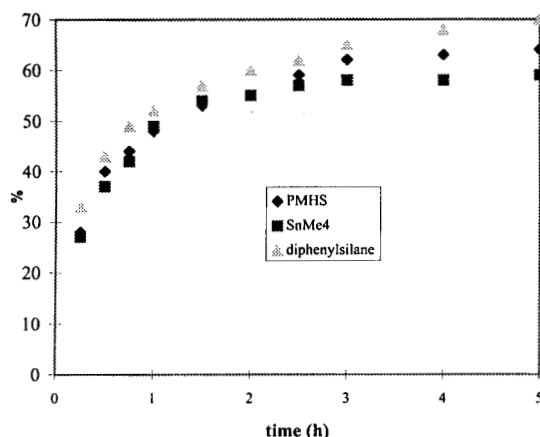


Figure 1. Conversion x time for the various catalytic systems in the reaction of methyl-10-undecenoate. Errors in the data points ranged from 0-5%.

Table 2. Metathesis of 10-undecenonitrile

System	ratio*	total conversion	selectivity	yield in dinitrile	yield in chloride
WCl <sub>6</sub> -PMHS	25:1:4	-	-	14%	1%
WCl <sub>6</sub> -PMHS	10:1:4	32% ± 3	72% ± 2	23% ± 2	9% ± 2
WCl <sub>6</sub> -PMHS	7:1:4	56%	60%	34%	22%
WCl <sub>6</sub> -PMHS	6:1:4	62%	65%	40%	22%
WCl <sub>6</sub> -Ph <sub>2</sub> SiH <sub>2</sub>	25:1:2	18%	76%	14%	4%
WCl <sub>6</sub> -Ph <sub>2</sub> SiH <sub>2</sub>	10:1:2	42% ± 3	62% ± 2	26% ± 3	16% ± 2
WCl <sub>6</sub> -SnMe <sub>4</sub>	10:1:4	40% ± 2	67% ± 2	28% ± 3	12% ± 3

\* nitrile:catalyst:co-catalyst.

of reaction is thought to work through the formation of a metal carbene, as shown in Scheme 1.

The purpose of the present work is to study the new catalytic system WCl<sub>6</sub>.PMHS, where PMHS = Me<sub>3</sub>SiO(MeHSiO)<sub>n</sub>SiMe<sub>3</sub>, n = 35 (polymethylhydrosiloxane), which avoids the use of the toxic SnMe<sub>4</sub> and Ph<sub>2</sub>SiH<sub>2</sub> in the metathesis reaction of methyl-10-undecenoate and 10-undecenonitrile. Therefore, direct comparison of this system to the known systems was carried out.

## Results

The ester:PMHS:WCl<sub>6</sub> ratio chosen for the present study was 25:4:1, which gave the best conversion factors in the preliminary study<sup>10</sup>.

The selectivity of the ester reaction was approximately 100%. Only when the reaction was performed on a large scale were traces of CH<sub>3</sub>CHCl(CH<sub>2</sub>)<sub>8</sub>COOCH<sub>3</sub> detected in addition to the expected product, as a result of adding HCl, formed in the reaction, to the double bond. The reactions were followed by <sup>1</sup>H-NMR spectroscopy since the olefinic protons showed signals at 4.8 (m) and 5.7 (m) ppm, for the starting ester, and at 5.25 (m) ppm for the diester. Integra-

Table 1. Conversion x time for the various catalytic systems in the reaction of methyl-10-undecenoate.

time (h)	Yield in diester (%)		
	WCl <sub>6</sub> -PMHS	WCl <sub>6</sub> -SnMe <sub>4</sub>	WCl <sub>6</sub> -Ph <sub>2</sub> SiH <sub>2</sub>
0.25	28 ± 4	27 ± 1	33 ± 3
0.50	40 ± 1	37 ± 7	43 ± 3
0.75	44 ± 3	42 ± 4	49 ± 3
1.00	48 ± 1	49 ± 3	52 ± 4
1.50	53 ± 0	54 ± 2	57 ± 5
2.00	55 ± 2	55 ± 2	60 ± 4
2.50	59 ± 3	57 ± 3	62 ± 3
3.00	62 ± 3	58 ± 3	65 ± 1
4.00	63 ± 4	58 ± 2	68 ± 2
5.00	64 ± 5	59 ± 2	70 ± 1

tion of these signals presented the conversion factors directly. The reaction carried out on the nitrile was analyzed according to the same criteria, taking into account the formation of the HCl-addition product.

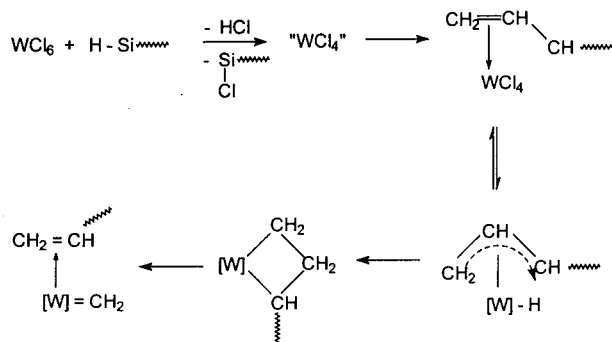
With either  $WCl_6$  or PMHS taken separately no reaction took place. The conversion factors, for the ester reaction with the catalytic system studied in this work are shown in Fig. 1 and Table 1. All the systems were very active at the beginning of the reaction but were deactivated after 2 h, probably as a result of the interaction of the catalytic species with the heteroatoms.

The results for the nitrile are shown in Table 2. The selectivity in this case was poorer than for the ester reaction (~100%), according to the literature for other catalytic systems. Analysis of the products, separated by silica-gel chromatography showed that in addition to 10-eicosenonitrile, 10-undecanonitrile chloride was also formed, as a result of adding HCl to the double bond.

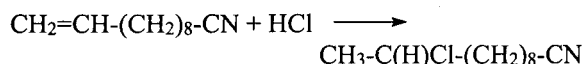
## Discussion

The new co-catalyst PMHS is a reductor under mild conditions which, however, does not reduce esters, amides or nitriles *per se*<sup>11</sup>. The results obtained show that the new system  $WCl_6$ .PMHS has activities strictly comparable to those of the other systems known for metathesizing esters and nitriles. Previous observations demonstrated that a prerequisite for the formation of an active catalyst was the presence of one or more Si-H bonds in the co-catalyst, and also, that upon interaction of  $Ph_2SiH_2$  with  $WCl_6$ , reduction took place, forming  $HCl^4$ . The present results confirm these observations. Moreover, the presence of Si-O bonds does not hinder the formation of the active species, the structure of which has yet to be established.

It seems, however, that PMHS as well as  $Ph_2SiH_2$  add to the metal through the Si-H bond with subsequent HCl elimination. This could lead to an active site on the metal. Posterior H-coordination of the olefin to the metal could generate the metal carbene:



The secondary product is found as:



Furthermore, the IR spectra (a shoulder appears in the  $\nu(C=C)$  band at lower energy) suggests a C=C coordination to the metal.

Finally, the new  $WCl_6$ .PMHS system presents results analogous to the well-defined  $WCl_6$ . $SnMe_4$  system with the previously noted advantages. These systems based on tungsten when compared to the ones based on rhenium present poorer results (the ratio substrate/Re for the ester is  $100/1^{3,9}$ ), but have the drawback of being more expensive than tungsten.

## Conclusion

Optimal working conditions for the very easy to use and inexpensive  $WCl_6$ .PMHS system were established for the metathesis reaction of functionalized olefins. The results can be favorably compared to the "classical" systems for the metathesis of this type of olefins, and it is particularly well-suited to the synthesis of simple starting difunctionalized olefins.

## Experimental

$WCl_6$ ,  $SnMe_4$ ,  $Ph_2SiH_2$  and PMHS were purchased from Aldrich Chemical Company. Methyl-10-undecenoate was kindly supplied by ATO Chimie (France). 10-undecenitrile was synthesized from the corresponding amide by refluxing it with thionyl chloride in benzene. The product was purified by vacuum distillation. The yield was 60%. 10-undecenitrile:  $^1H-NMR$  ( $\delta$ , in  $CDCl_3$ ) 1.34 (m, 10H), 1.70 (m, 2H), 2.04 (m, 2H), 2.38 (t, 2H), 4.98 (t, 2H), 4.98 (t, 2H), 5.82 (m, 1H); MS (EI, 70 eV)  $m/z$  165 (M), 136 (M -  $C_2H_5$ ), 122 (M -  $C_3H_7$ ); IR  $\nu_{max}$  ( $cm^{-1}$ ) 2242 ( $C\equiv N$ ) 1635 ( $C=C$ ). 10-undecenoamide was synthesized by a reaction of 10-undenoyl-chloride (Aldrich) with  $NH_4OH^4$ . All of the metathesis reactions were performed under an argon atmosphere in a glove box.

In a typical reaction, 127 mg of  $WCl_6$  was added to a flask containing 1.59 g of degassed methyl-10-undecenoate at 75 °C, followed by the addition of 0.081 g of degassed PMHS, making the ester: $WCl_6$ :PMHS ratio 25:1:4. For the nitrile, the ratio was 10:1:4 and the temperature 100 °C. The bubbling of argon into the solution was necessary in order to carry the HCl and  $C_2H_4$  and drive the reaction to the product. The samples collected for analysis were diluted with  $Et_2O$ , filtered in microcolumns with celite 545 and analyzed by  $^1H-NMR$  spectroscopy. All products were characterized by mass spectroscopy, IR and  $^1H-NMR$  spectroscopies: methyl 10-undecanoyl chloride:  $^1H-NMR$  ( $\delta$ , in  $CDCl_3$ ) 1.3 (m, 12H), 1.4 (d, 3H), 1.6 (m, 2H), 2.2 (t, 2H), 3.6 (s, 3H), 3.9 (m, 1H); MS (EI, 70 eV) 203 (M), 166 (M -  $CH_3O$ ); IR  $\nu_{max}$  ( $cm^{-1}$ ) 1737 ( $C=O$ ), 1736 ( $CH_3$ ). dimethyl 10-eicosenoate:  $^1H-NMR$  ( $\delta$ , in  $CDCl_3$ ) 2.4 - 1.2 (m, 32H), 3.6 (s, 6H), 5.25 (m, 2H); MS (EI, 70 eV) 368 (M); IR  $\nu_{max}$  ( $cm^{-1}$ ) 1734 ( $C=O$ ). 10-undecanonitrile chloride:  $^1H-NMR$

( $\delta$ , in  $\text{CDCl}_3$ ) 1.25 (m, 10H), 1.55 (d, 3H), 1.62 (m, 4H), 2.30 (t, 2H), 3.92 (m, 1H); MS (EI, 70 eV) 201 (M), 164 (M -  $\text{H}_2\text{Cl}$ ); IR  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 2245 ( $\text{C}\equiv\text{N}$ ), 1378 ( $\text{CH}_3$ ). 10-eicosenodinitrile:  $^1\text{H-NMR}$  ( $\delta$ , in  $\text{CDCl}_3$ ) 1.30 (m, 20H), 1.68 (m, 4H), 2.0 (m, 4H), 2.35 (t, 4H), 5.4 (m, 2H); MS (EI, 70 eV) 302 (M); IR  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 2250 ( $\text{C}\equiv\text{N}$ ).

All NMR spectra were performed on a VARIAN CXR 200 MHz spectrometer using  $\text{CDCl}_3$  or  $\text{CCl}_4$  as solvents. The IR data were taken in a Perkin-Elmer 1430 coupled with a 483 data station. The spectra were obtained as liquid films in CsI cells. The mass spectra were made in a HP 5988 A mass spectrometer coupled with a HP 590 GC.

The conversion factors (C) were estimated from the integration of the olefinic proton signals by the equation  $C = 2D/(E_2 + 2D)$ , where D = integration of the diester or dinitrile olefinic proton signals and  $E_2$  = integration of the two terminal ester or nitrile olefinic proton signals. Tests with a calibrated solution confirmed an error of 4%. Turnover numbers were calculated by  $\text{TN} = 25C/2$  for the ester, assuming a selectivity close to 100%, and  $\text{TN} = \text{excess olefin} \times (\text{C}_{\text{dinitrile}}/2 + \text{C}_{\text{chloride product}})$ , for the nitrile, as the selectivity was not close to 100%. The chloride product was estimated from the  $^1\text{H-NMR}$  signal of the proton at 3.9 ppm. All the reactions were repeated at least three times, and all the data points reflect the average of the reactions.

### Acknowledgments

The authors thank CNPq-Brazil and FAPERGS-Brazil for financial support, and CNPQ and CAPES for fellowships for J.R.G and C.K.

### References

1. Ivin, K.J.; *Olefin Metathesis*; Academic Press; New York, 1982.
2. Grubbs, R.H.; *Comprehensive Organometallic Chemistry* In Wilkinson, Ed.; Pergamon, Oxford, 1982; vol 8, p 499.
3. Mol, J.C. In Anderson, J.R.; Boudart, M., Eds; *Catalysis Science and Technology, Catalytic Metathesis of Alkenes*; Springer Verlag; Berlin, 1987; vol 8.
4. Levisalles, J.; Rudler, H.; Cuzin, D.; Rull, T.; *J. Mol. Cat.* **1984**, *26*, 231.
5. Mol, J.C.; Woerlee, E.F.G.; *J. Chem. Soc., Chem. Commun.* **1979**, 330.
6. Schaverien, C.J.; Dewan, J.C.; Schrock, R.R.; *J. Am. Chem. Soc.* **1986**, *108*, 2771.
7. Fu, G.C.; Grubbs, R.H.; *J. Am. Chem. Soc.* **1992**, *114*, 5426.
8. Ehrenfeld, D.; Kress, J.; Moore, B.D.; Osborn, J.A.; Schoettel, G.; *J. Chem. Soc., Chem. Commun.* **1987**, 129.
9. Hermann, W.A.; Wagner, W.; Flessner, U.N.; Volkhardt, V.; Komber, H.; *Angew. Chem. Int. Ed. Engl.* **1991**; *30*, 1636.
10. Baibich, I.M.; Rudler, H.; 5<sup>o</sup> Seminário Brasileiro de Catálise, Guarujá-SP, Brazil; 1989.
11. Lipowitz, J.; Bowman, S.A.; *J. Org. Chem.* **1973**, *38*, 162.