

To be of practical use a recyclable polymer-linked catalyst has to fill several criteria: (i) the clean synthesis of the supported catalyst to avoid the presence of polymeric impurities, (ii) the weak decrease of catalytic activity induced by the polymeric matrix, (iii) an efficient technique of catalyst recovery, and (iv) the retention of activity after several recycles.

The anchoring of an homogeneous catalyst to a polymeric support is a general approach to obtain supported catalyst [4,5]. However, as the fixation of a catalytic species to a polymer is never complete, the presence of some remaining free macromolecules leads to a decrease of the catalyst activity. The polymerization of a monomeric catalyst [6] is an alternative to generate a supported catalyst with some key advantages such as the control of the concentration in metal fragment or the nature of the polymer matrix (hydrophobic, hydrophilic, polar...) by using adapted organic comonomers.

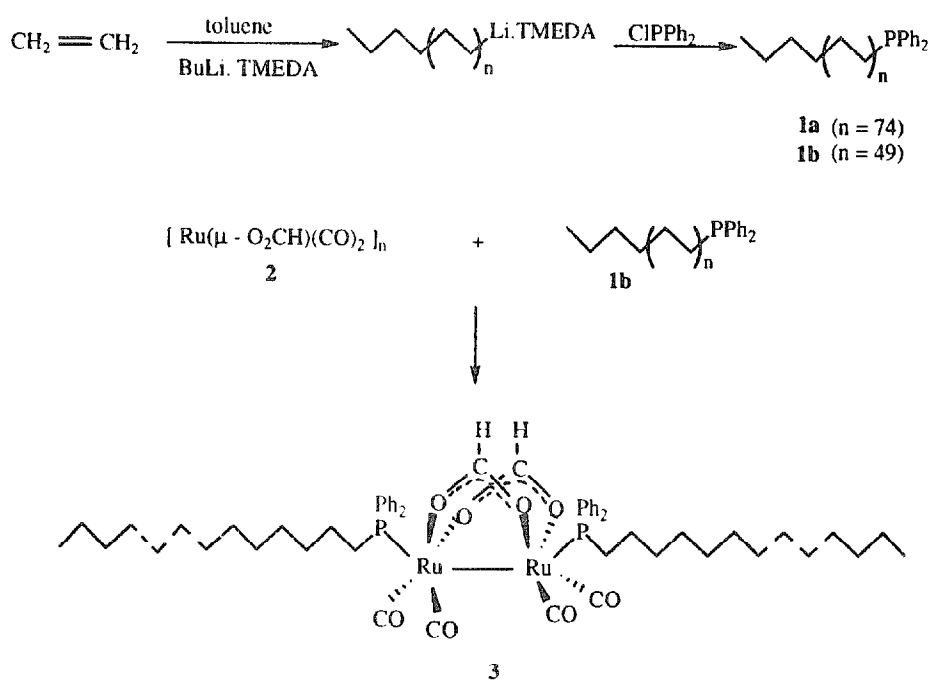
The homogeneous catalyst $[\text{Ru}(\mu\text{-O}_2\text{CH})(\text{CO})_2(\text{PPh}_3)_2]$ **A** has appeared to be one of the most efficient catalyst for the generation of enol esters (Eq. 1 (a)) and for the catalytic synthesis of dioxolanones by addition of man-

delic acid to terminal alkynes [7]. As catalyst **A** was lost during the purification steps we attempted to anchor this catalyst on a polymeric phosphine leading to a soluble catalyst at reaction temperature, thus homogeneous, but insoluble at room temperature to favor the recovery.

We report here (i) the synthesis of a new binuclear ruthenium catalyst $[\text{Ru}(\mu\text{-O}_2\text{CH})(\text{CO})_2[\text{PPh}_2(\text{PE})]]_2$ **3** containing a diphenylphosphinated polyethylene ligand $\text{PPh}_2(\text{PE}) = \text{PPh}_2(\text{CH}_2\text{CH}_2)_n\text{CH}_2\text{CH}_3$, (ii) the catalytic properties of **3**, soluble in toluene at 100°C , towards the synthesis of a dioxolanone and enol diesters at 100°C , and (iii) the easy recycling of catalyst **3** and retention of its efficiency after six recycles.

2. Results and discussion

The polymeric phosphines **1** have been prepared by anionic polymerization of ethylene followed by quenching with chlorodiphenylphosphine [8]. A solution of *n*-butyllithium/TMEDA (16 mmol/16 mmol) in hexane (250 ml) was stirred at room tempera-



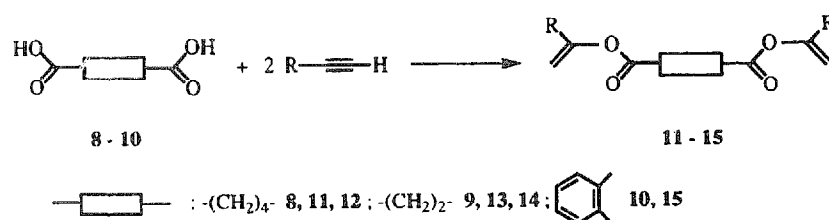
Scheme 1.

The solution became homogeneous and was stirred for 20 h. After cooling at 25°C, the catalyst **3** was separated by filtration from the solution. The purification of the crude product by vacuum transfer gave 83% of pure dioxolanone **7** and both the enol ester intermediate **6** and the starting carboxylic acid were absent. Complex **3** thus provides a similar activity as **A** (84% of **7** for 20 h at 100°C [7]) but with a lower diastereoselectivity (*cis/trans* = 5/1 (**3**) and 9/1 (**A**)). This lower diastereoselectivity in the metal-assisted intramolecular cyclization (**6** → **7**) with supported catalyst **3** could be due to

a different steric hindrance induced by the presence of the polyethylene chain.

4. One-step catalytic synthesis of activated enol diesters

The ruthenium containing oligomer **3** was used as a catalyst to activate terminal alkynes towards the addition of carboxylic diacids **8–10** and produce new enol diesters **11–15** according to Eq. 3.

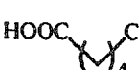
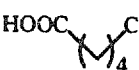
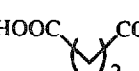
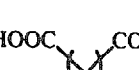
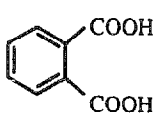


(3)

In a typical procedure a carboxylic diacid (10 mmol) and 2 equivalents of terminal alkyne were mixed with catalyst **3** (0.36 g, 0.1 mmol)

in 20 ml of toluene. The heterogeneous mixture at room temperature became totally homogeneous at 100°C. After 20 h at 100°C, the solu-

Table 1
Catalytic synthesis of enol diesters **11–15**

Run	Diacid	R $\text{---} \text{C} \equiv \text{C} \text{---} \text{H}$	Enol diesters (yield %)
1	HOOC  COOH 8	nBu $\text{---} \text{C} \equiv \text{C} \text{---} \text{H}$	11 (94)
2	HOOC  COOH 8	Me $\text{---} \text{C} \equiv \text{C} \text{---} \text{H}$	12 (84)
3	HOOC  COOH 9	nBu $\text{---} \text{C} \equiv \text{C} \text{---} \text{H}$	13 (84)
4	HOOC  COOH 9	Me $\text{---} \text{C} \equiv \text{C} \text{---} \text{H}$	14 (77)
5	 10	nBu $\text{---} \text{C} \equiv \text{C} \text{---} \text{H}$	15 (53)

tion was cooled to room temperature and the suspension of the polymeric catalyst was filtered and the catalyst was washed with methanol, dried and identified to catalyst **3** by infrared spectroscopy. *The recovered catalyst can be reused for another similar experiment.* The solvent was removed from the solution and the crude product was purified by distillation. No carboxylic diacid was detected indicating its complete transformation and, as revealed by electronic microscopy analysis of the residue, no ruthenium was left after filtration of the catalyst at room temperature.

Thus catalytic addition of adipic **8**, succinic **9** and phthalic **10** acids to hex-1-yne and prop-1-yne were investigated and led to the selective formation of diesters **11–15** in 53–94% yield. The results are reported in Table 1. In experiments 4 and 5 (Table 1) the lower yields in enol diesters **14** and **15** were obtained because succinic and phthalic anhydride were formed in 20% and 33%, respectively as secondary products. The latter likely resulted from the intramolecular reaction of one carboxylic group with one enol ester group of the intermediate with elimination of ketone.

All enol diesters **11–15** were fully characterized by elemental analysis and spectroscopic data. Only derivatives resulting from the Markovnikov addition of the carboxylate were isolated, as indicated by gas chromatography analysis and ^1H NMR spectroscopy ($\text{C}=\text{CH}_2$ at $\delta \sim 4.6$ ppm) or ^{13}C NMR ($\text{C}=\text{CH}_2$ at $\delta \sim 101$ ppm and $\text{C}=\text{CH}_2$ at $\delta \sim 156$ ppm). Only traces of Z or E compounds resulting from the addition at the C_1 carbon of terminal acetylenic substrates were detected. This means that the addition of the carboxylate is highly selectively oriented at the C_2 carbon of the alkyne by catalyst **3**.

5. Recycling of polymeric catalyst **3**

The separation of the catalyst **3** from the reaction products is easily achieved by simple

filtration. The recycling of **3** is also efficient as the retention of activity of catalyst **3** was observed after several catalytic reactions and recoveries. For example, experiment 1 (Table 1) was performed seven times without significant loss of yield or selectivity in the formation of **11**. No darkening of the solution of recovered **3**, corresponding to the formation of colloidal $\text{Ru}(0)$, was observed after repeated uses. Infrared indicated no significant changes of catalyst **3** after six recycles.

Moreover, it is possible to use the same recovered catalyst **3** for different catalytic reactions. For example no modification of activity was detected during the two following sequences: run 2 \rightarrow run 3 \rightarrow run 2 \rightarrow run 3 \rightarrow run 2 \rightarrow run 4 \rightarrow run 4, and run 1 \rightarrow run 5 \rightarrow run 5 \rightarrow run 1. These experiments show the possibility to work with different carboxylic diacids (aliphatic or aromatic) and different terminal alkynes with only one sample of catalyst **3**. In other words, the same sample of catalyst **3** (0.36 g, 0.1 mmol) was able to produce 55 mmol of diesters **12–14** in the seven reactions along the first sequence.

6. Conclusion

These results show that the catalytic properties of the ruthenium fragment are not perturbed by the presence of the polymeric ligand in $[\text{Ru}(\mu\text{-O}_2\text{CH})(\text{CO})_2(\text{PPh}_2(\text{CH}_2\text{CH}_2)_n\text{CH}_2\text{CH}_3)]_2$ which offers a direct access to enol diesters. The retention of activity, regioselectivity and stability of the catalyst over several cycles allows a large scale, cheap access to enol diesters which can be used as activated diesters.

References

- [1] C. Bruneau, M. Neveux, Z. Kabouche and P.H. Dixneuf, *Synlett*, (1991) 755–763.
- [2] M. Neveux, C. Bruneau and P.H. Dixneuf, *J. Chem. Soc., Perkin Trans. 1*, (1991) 1197–1199.

- [3] Z. Kabouche, C. Bruneau and P.H. Dixneuf, *Tetrahedron Lett.*, 32 (39) (1991) 5359–5362.
- [4] Y. Chauvin, D. Commereuc and F. Dawans, *Progr. Polym. Sci.*, 5 (1977) 95–226.
- [5] C.U. Pittman Jr, *Compr. Organomet. Chem.*, 8 (1982) 553–611.
- [6] O. Lavastre, P.H. Dixneuf, A. Pacreau and J.-P. Vaiton, *Organometallics*, 13 (1994) 2500–2503.
- [7] M. Neveux, B. Seiller, F. Hagedorn, C. Bruneau and P.H. Dixneuf, *J. Organomet. Chem.*, 451 (1993) 133–138.
- [8] D.E. Bergbreiter and R. Chandran, *J. Am. Chem. Soc.*, 109 (1987) 174–179.
- [9] G.R. Crooks, B.F.G. Johnson, J. Lewis and I.G. Williams, *J. Chem. Soc. A.* (1969) 2761–2766.
- [10] O. Lavastre and P.H. Dixneuf, *J. Organomet. Chem.*, 488 (1995) C9–C10.