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Recyclable polymeric phosphine-ruthenium catalyst for the synthesis of new enol diesters

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Abstract

The synthesis of a ruthenium containing catalyst linked to a polymeric phosphine, $[Ru(\mu - O_2CH)(CO)_2(PPh_2(CH_2CH_2)_{50}CH_2CH_3)]_2$, is described. The polyethylene chain induced a temperature dependent solubility of the ruthenium catalyst which was soluble in toluene at 100°C but insoluble at room temperature. This property was used for an efficient technique of catalyst recovery. Catalytic properties of the complex was shown in the synthesis of a dioxolanone and for the large scale access to several new enol diesters via the activation of terminal alkynes towards addition of carboxylic acids. The recycling of the supported ruthenium catalyst was performed without loss of activity.

Keywords: Ruthenium; Polymeric phosphine; Phosphine; Recyclable catalyst; Enol diester; Alkyne activation

1. Introduction

Ruthenium complexes have been shown to act as efficient homogeneous catalysts for the regioselective Markovnikov-type addition of carboxylic acids to alkynes to produce enol esters in high yields [1]. The latter constitute excellent acylation reagents of amines and alcohols [2,3] under very mild conditions, with release of a volatile ketone as the only by-product (Eq. 1). The overall process could be used for the large scale synthesis of activated enol diesters, potential polymer precursors on reaction with diamines or diols, if the recovery of the ruthenium catalyst could be achieved, even if efficient ruthenium catalysts are not that very expensive.



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To be of practical use a recyclable polymerlinked 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 $[Ru(\mu - O_2CH)(CO)_2(PPh_3)]_2$ 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 $[Ru(\mu - O_2CH)(CO)_2[PPh_2(PE)]]_2$ 3 containing a diphenylphosphinated polyethylene ligand PPh₂(PE) = PPh₂(CH₂CH₂)_nCH₂CH₃, (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 nbutyllithium/TMEDA (16 mmol/16 mmol) in hexane (250 ml) was stirred at room tempera-



ture under a constant pressure of 2 bar of ethylene. A white precipitate appeared and, after 30 h, the resulting lithiated polyethylene oligomers were quenched with $ClPPh_2$ in excess (32 mmol). After purification a white powder (7 g) of **1a** was obtained (Scheme 1).

The ³¹P NMR spectrum of **1a**, in toluene-d₈ at 100°C, showed only a singlet at $\delta = -13.9$ ppm corresponding to a diphenyl phosphinated polyethylene (no signal at $\delta \sim 36$ ppm corresponding to phosphine oxide was observed [8]). The loading of Ph₂P end groups was estimated by 'H NMR spectroscopy. A sample of phosphine 1a in the presence of a weighed amount of ferrocene, in toluene-d₈ at 100°C, allowed the determination, via integration, of the $Ph_2P/Fe(C_5H_5)_2$ ratio, and consequently that 1 g of phosphine 1a contains approximately 0.4 mmol of Ph₂P groups. This measurement is consistent with an average molecular mass $M_{\rm n}$ = 2300, corresponding to the formula $CH_3CH_2(CH_2CH_2)_{75}PPh_2$, and elemental analysis.

As in living ethylene polymerization the length of the chain increases with the reaction time under constant pressure of ethylene, a polyethylene phosphine 1b containing a shorter polyethylene chain was prepared analogously to 1a, but the quenching with ClPPh₂ was performed after 17 h at room temperature. 1b was obtained (7.6 g) and identified as $CH_3CH_2(CH_2CH_2)_{50}PPh_2$ ($M_n = 1600$, 0.63 mmol of Ph₂P groups per gram of polymer).

The preparation of a complex similar to $[Ru(\mu-O_2CH)(CO)_2PPh_3]_2$ but with a long hy-

drocarbon chain containing phosphine **1b** was attempted via a modified procedure of that leading to $[Ru(\mu-O_2CH)(CO)_2PPh_3]_2$ [9]. $[Ru(\mu O_2$ CH)(CO)₂]_n 2 [9] (1.5 mmol of Ru atoms), polymeric phosphine 1b (1.5 mmol of PPh, groups) in methylcyclohexane were stirred at 100°C in a homogeneous solution for 3 h. The filtration at room temperature and washing of the solid with diethyl ether led to the isolation of a yellow powder identified as complex 3 (95% yield) (Scheme 1). The infrared spectrum of 3 showed absorptions at ν (cm⁻¹) = 2026 (m), 1983 (w), 1954 (m) for carbonyl ligands and at 1595 cm⁻¹ for the μ -formate bridging ligand [9]. The ³¹P NMR spectrum of 3 (toluene-d₈, 100°C) showed only one singlet at $\delta = 11.96$ ppm consistent with a coordinated phosphine ligand. No signal for the uncoordinated phosphine 1b ($\delta = -13.9$ ppm) was observed. The NMR and the elemental analysis of 3 was in agreement with the coordination of one phosphine to each ruthenium atom [Ru(μ - $O_{2}CH(CO)_{2}(PPh_{2}(CH_{2}CH_{2})_{50}CH_{2}CH_{3})]_{2}$.

3. Catalytic properties of polymeric catalyst 3

The catalytic efficiency of 3 was compared to that of $[Ru(\mu-O_2CH)(CO)_2PPh_3]_2$ A in the synthesis of dioxolanone 7 from the α -hydroxy carboxylic acid 4 and hex-1-yne 5 [7] (Eq. 2). This reaction was difficult to perform and among a variety of ruthenium catalysts, only the latter complex A and an alkenyl-ruthenium precursor [10] were shown to be efficient.



(2)

The heterogeneous mixture of R-(-)mandelic acid 4 (10 mmol), hex-1-yne 5 (10

mmol), and supported catalyst 3 (0.36 g, 0.1 mmol) in 10 ml of toluene was heated at 100° C.

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 \rightarrow 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 e-ool 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 — H	Enol diesters (yield %)
1	ноос соон	8	nBu ~ ≕-H	11 (94)
2	ноос соон	8	Me -=- H	12 (84)
3	ноос соон	9	nBu ≕ -H	13 (84)
4	ноос соон	9	Me- H	14 (77)
5	СООН	10	nBu- H	15 (53)

tion was cooled to room temperature and the suspension of the polymeric catalyst was filtrated 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-1yne 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 (C=CH₂ at $\delta \sim 4.6$ ppm) or ¹³C NMR (C=CH₂ at $\delta \sim 101$ ppm and C=CH₂ at $\delta \sim 156$ ppm). Only traces of Z or E compounds resulting from the addition at the C₁ carbon of terminal acetylenic substrates were detected. This means that the addition of the carboxylate is highly selectively oriented at the C₂ 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 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 $[Ruu(\mu)$ $O_2CH)(CO)_2(PPh_2(CH_2CH_2)_nCH_2CH_3)]_2$ 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.

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