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Ring-opening polymerisation of norbornene by $(\mu\text{-H})_2Os_3(CO)_{10}$ complex

S. Aime* [a,1], A.J. Arce* [b,2], O. Chiantore [a], R. Gobetto [a], A. Russo [a], Y. De Sanctis [b]

[a] *Dipartimento di Chimica I.F.M., Università di Torino, Via Pietro Giuria 7, 10125 Turin, Italy*
[b] *Centro de Quimica, Instituto Venezolano de Investigaciones Cientificas (IVIC), Apartado 21827, Caracas 1020-A, Venezuela*

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Abstract

The $(\mu\text{-H})_2Os_3(CO)_{10}$ catalyses the ring opening polymerisation of norbornene to give high molecular weight poly (1,3-cyclopentylene-vinylene) in high yield. Initially IR and ^{13}C-NMR data reveal the presence of an all *cis* structure of the polymer, whereas for longer reaction times there is a progressive increase in the *trans* content. A reaction mechanism for the polymerisation is proposed involving the formation of a dimetallacyclopentene intermediate. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ring-opening polymerisation; Norbornene; Osmium complexes

1. Introduction

In recent years, there has been much interest in the preparation of polymers with well defined molecular architectures by the ring opening metathesis polymerisation (ROMP) of norbornene derivatives [1–3]. Polynorbornene shows interesting physical properties that have been suggested for different industrial applications [4,5] such as, for example, cleaning up oceanic oil spills or vibration dampening in engines. The resulting polymers obtained by ROMP of norbornene contain enchained bonds and rings in which the double bonds may be *cis* or *trans* depending on the catalyst. Detailed information on *cis*/*trans* blockiness, as well as tacticity has been obtained [6–8] by ^{13}C-NMR spectroscopy. A great number of highly active transition metal catalysts have been evaluated, some of them operating also in ethanolic solution and in aqueous emulsion [9–13]. Several Os containing complexes are active ROMP catalyst: $OsCl_3$ [14] and (*p*-cimene)$OsCl_2P(c\text{-}H_x)_3$ [15] have been reported to be good catalysts for norbornene polymerisation, but also alumina supported OsO_2 was found to have ROMP activity [16]. Recently Brumaghim and Girolami [17] demonstrated that the dinuclear complex $Cp^*_2Os_2Br_4$ (Cp* = penta-methylcyclopentadienyl) with methylaluminoxane is able to produce 167 kg of polynorbornene per mol of catalyst at room temperature. This observation prompted us to investigate the catalytic activity of other osmium containing species.

The unsaturated 46e$^-$ cluster $(\mu\text{-H})_2Os_3(CO)_{10}$ has been the subject of several studies concerning reactions towards nucleophiles [18], electrophiles [19], insertion reactions [20]. Insertion of alkenes into $(\mu\text{-H})_2Os_3(CO)_{10}$ gives $Os_3(\mu\text{-H})$ (alkenyl)$(CO)_{10}$ compounds which usually are reactive towards β-elimination to regenerate the alkene, or reductive elimination of the alkane to allow oxidative addition of the alkene [21]. $(\mu\text{-H})_2Os_3(CO)_{10}$ also catalyses the formation of hexaphenylbenzene from diphenylacetylene [22]; the whole sequence of reactions leading to C_6Ph_6 was established, but they may, of course, not correspond to the catalytic route.

We describe here a preliminary account on the use of a 46e$^-$ compound $(\mu\text{-H})_2Os_3(CO)_{10}$ to promote the ring-opening polymerisation of strained molecules such as norbornene. To the best of our knowledge, this is the first example of ROMP of norbornene catalysed by a transition metal carbonyl cluster.

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[1] *Corresponding author. Tel.: +39-11-6707520; fax: +39-11-6707524; e-mail: aime@ch.unito.it

[2] *Corresponding author.

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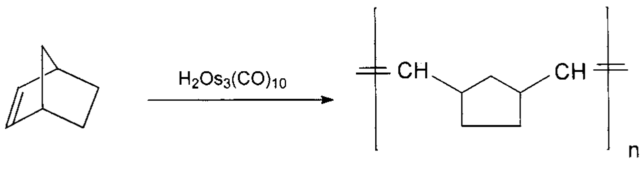
2. Experimental

All reactions were carried out using standard Schlenk line techniques under nitrogen. The cluster $(\mu\text{-H})_2Os_3(CO)_{10}$ was prepared as previously described and recrystallised from a pentane solution [23]. The $^{13}C\{^1H\}$-NMR spectra were recorded on a JEOL EX-400 (^{13}C 100 MHz) spectrometer in $CDCl_3$ or $(CD_3)_2CO$ solution. IR data were acquired on a Perkin–Elmer 580 B.

2.1. General procedure for the polymerisation of norbornene

Norbornene (0.2 g, 2 mmol) and crystals of $(\mu\text{-H})_2Os_3(CO)_{10}$ (0.004 g, 400 μmol) were dissolved in CH_2Cl_2 and stirred at room temperature (r.t.) for 2 h under nitrogen, the viscosity of the solution increasing gradually. The reaction was monitored by IR and ^{13}C-NMR spectroscopy. Through out the reaction the colour remained unchanged. At the end of the reaction the solvent was removed under vacuum and the $(\mu\text{-H})_2Os_3(CO)_{10}$ was almost quantitatively recovered by extracting from the polymer material with pentane. The polymer, as a white fibrous material, was collected by filtration and dried in vacuum. Molecular weights were determined by a gel permeation chromatography (GPC) system equipped with 3 Pl-Gel linear columns.

Columns calibration was performed with polystyrene narrow distribution standards. The column were eluted with distilled THF at a flow rate of 1 ml min^{-1}, and a sample injection volume was 200 μl of a 0.2% (w/v) of polymer dissolved in THF.



Scheme 1.

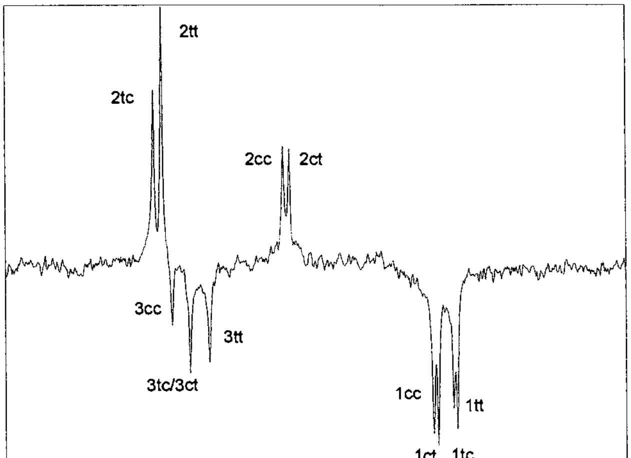


Fig. 1. Distorsionless enhancement by polarization transfer (DEPT) ($\theta = 3\pi/4$) ^{13}C-NMR spectra of poly (1,3 cyclopentylenevinylene) in $CDCl_3$ using $(\mu\text{-H})_2Os_3(CO)_{10}$ as a catalyst after 6 h at room temperature.

3. Results and discussion

When the 46e$^-$ complex $(\mu\text{-H})_2Os_3(CO)_{10}$ in CH_2Cl_2 was treated with 50 equivalents of norbornene the viscosity of the solution increased gradually indicating that polymerisation had occurred. After work up procedure, a white fibrous material characterised as poly(1,3-cyclopentylenevinylene) was obtained in 80% yield (Scheme 1). IR spectroscopy showed the presence of a broad band centered at 2900 cm^{-1} assigned to the stretching of C–H bonds, three main bands at 1778, 1712 and 1650 due to the stretching of C=C double bonds and several bands in the finger prints region. For longer reaction times, the band at 740 cm^{-1}, assigned to the bending mode of the *cis* disubstituted double bonds, was progressively replaced by a peak at 968 cm^{-1} consistent with an increasing *trans* disubstituted content. On monitoring the reaction by $^{13}C\{^1H\}$-NMR a similar result was obtained: an initially peak at δ 134.3 dominated the olefinic region of the spectrum (this is consistent with the previously reported results). The microstructure of the polymer is less regular if the polymerisation is allowed to proceed for longer reaction times: six different peaks can be detected, respectively at δ 134.4 (tcc), 134.3 (tct, ccc), 134.2 (cct), 133.5 (ttc), 133.4 (ttt, ctc), 133.2 (ctt) for the olefinic carbons. The formalism used here to designate particular olefinic carbons is the same as reported in the Ref. [8]. The assignment has been obtained in agreement with the literature data and confirmed using DEPT ($\theta = 3\pi/4$) ^{13}C-NMR spectra (see Fig. 1). Accurate determination of the relative amounts of *cis* and *trans* double bond contents has been obtained by peak fitting of the ^{13}C-NMR spectra. After long reaction times (5 days) the *trans* component is largely dominant in the polymer, since the *trans*:*cis* ratio is 12:1.

The polymer formed had a high molecular weight as revealed by GPC (see Table 1). It is worth noting that although polydispersity is bigger than in other homogeneous systems [24] the high stereo regularity is remarkable. In order to test the catalytic activity we treated, at r.t., a solution of $(\mu\text{-H})_2Os_3(CO)_{10}$ with 1000 equivalents of norbornene and after 18 h the polymer obtained was collected by filtration and dried in vacuum. Under this conditions we obtained 14.2 kg of polynorbornene per mol of catalyst, This result indicates that

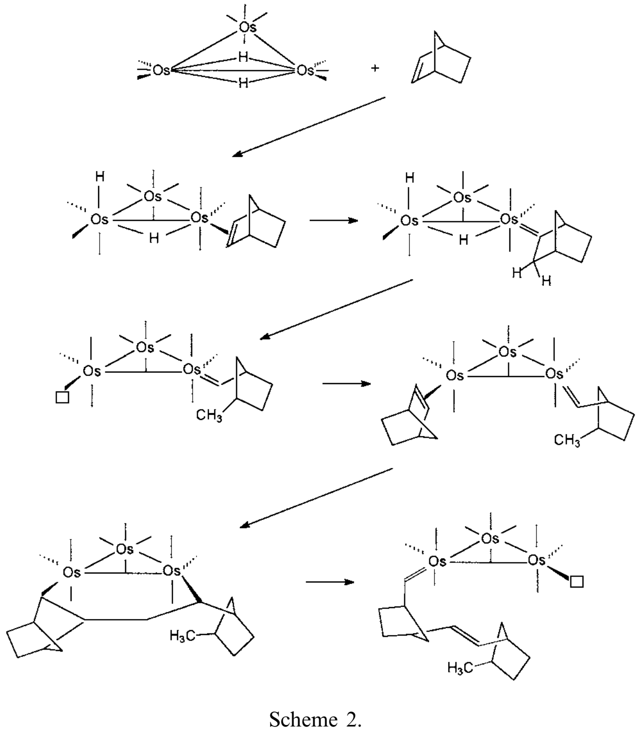
Table 1

Compound	Yield (%)	Mn (10^6)	Mw (10^6)	PDI	Ref.
$(\mu\text{-H})_2Os_3(CO)_{10}$	95	0.152	0.4336	2.84	This work
$Mo(\eta\text{-}C_7H_7)(PPh_3)I_2$	68	1.8	2.2	1.25	[24]
$W(\eta\text{-}C_7H_7)(MeCN)I_2$	92	0.239	0.380	1.59	[24]

the rate of norbornene polymerisation with $(\mu\text{-H})_2Os_3(CO)_{10}$ is less but still comparable with that of other Os containing catalysts (15.4 kg mol^{-1} of catalyst for Cp*Os(COD)Br, 30.3 kg mol^{-1} of catalyst for $Cp^*2Os_2Br_4$) [17].

Attempts to polymerise other strained molecules such as cyclopentene, cyclohexane, cyclooctene with $(\mu\text{-H})_2Os_3(CO)_{10}$ were unsuccessful since only insertion products were obtained that were fully characterised by IR and NMR spectroscopy [25]. The mechanism of the ring-opening polymerisation of norbornene with $\mu\text{-}H_2Os_3(CO)_{10}$ probably involves the co-ordination of norbornene to the unsaturated cluster to form an intermediate of formula $(H)Os_3(\mu\text{-H})(CO)_{10}$(norbornene) that is in equilibrium with a carbene complex. The reaction may proceed through the formation of a vacant site on the neighbouring Os atom as shown in Scheme 2, where a new norbornene molecule can be co-ordinated with the subsequent formation of a dimetallacyclopentene intermediate. Due to steric requirements, it is likely that after a few step the polymer co-ordinates in a *trans* way instead of a *cis* one.

Attempts to isolate the active osmium carbene complex directly from ROMP reaction were unsuccessful. The propagating species was not observed either by carrying out polymerisation in NMR tubes by using ^{1}H-NMR spectroscopy, probably due to its low concentration. However the ^{1}H-NMR spectrum shows the presence of two signals at δ 9.6 and -14.79 ppm that suggest the formation of a species of formula $HOs_3(CO)_{10}(\sigma,\pi\text{-norbornene})$ due to a side reaction of the unsaturated $H_2Os_3(CO)_{10}$ species with free norbornene.



Scheme 2.

4. Conclusions

The above observations demonstrate that also transition-metal cluster are viable catalysts in the ROMP of bicyclic monomers. The potential for ligand modification in the cluster holds great promise for fine-tuning the reactivity of the catalyst. This may form the basis for further development of ROMP catalysts based on $H_2Os_3(CO)_9L$ (where $L = CO$, PPh_3, $AsPh_3$, *t*-BuNC etc.) which are all well-defined in terms of structure and may offer higher reactivity, selectivity and perhaps better tolerance of a wide range of functionality.

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