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$OsHCl(CO)(P^iPr_3)_2$ as catalyst for ring-opening metathesis polymerization (ROMP) and tandem ROMP–hydrogenation of norbornene and 2,5-norbornadiene

Noelia Cobo,[a] Miguel A. Esteruelas,[b,*] Fernando González,[a] Juana Herrero,[a] Ana M. López,[b]
Patricia Lucio,[a] and Montserrat Oliván [b]

[a] *Departamento de Ingeniería Química y Química Inorgánica, Universidad de Cantabria, 39005 Santander, Spain*
[b] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, C.S.I.C., 50009 Zaragoza, Spain*

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Abstract

Complex $OsHCl(CO)(P^iPr_3)_2$ catalyzes the ring-opening metathesis polymerization (ROMP) of norbornene and 2,5-norbornadiene to give poly(norbornene) and poly(norbornadiene), respectively. In both cases the resulting polymers have a high *cis* (74–95%) content. The stereoregularity or tacticity of the cyclopentane and cyclopentene ring sequences in poly(norbornene) and poly(norbornadiene) estimated from the $^{13}C\{^1H\}$ NMR spectra of the hydrogenated derivatives was found to be syndiotactic. Complex $OsHCl(CO)(P^iPr_3)_2$ is also active in tandem ROMP–hydrogenation of norbornene and 2,5-norbornadiene. At 40 °C and 3 atm of H_2, poly(norbornene) is fully hydrogenated in 48 h, while poly(norbornadiene) is fully hydrogenated in 48 h at 75 °C and 3 atm of H_2. The complex $RuHCl(CO)(P^iPr_3)_2$ is also active in ROMP and tandem ROMP–hydrogenation of norbornene, obtaining *trans*-poly(norbornene) and hydrogenated poly(norbornene), respectively.

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1. Introduction

Homogeneous transition-metal catalysts are usually designed to mediate a single reaction. However, the increasing demand for advantageous and efficient synthetic processes requires the development of tandem catalysis, in which one catalyst supports several functions, with two, or more, mechanistically distinct reactions being accomplished by the same organometallic reagent directly or by simple modification.

Ring-opening metathesis polymerization (ROMP) of cyclic olefins is a powerful tool for polymer chemistry [1–3]. A common feature of all polymers produced via metathesis is unsaturation in the main chain, which limits their applications by the susceptibility of the carbon–carbon double bonds to oxidative and thermal degradation. Therefore, hydrogenation of metathesis polymers is important to widen their range of applications [4]. ROMP of cyclic olefins, followed by hydrogenation, allows the synthesis of lightweight, moldable polymers with desirable optical characteristics [5,6].

At present, metathesis polymers are typically prepared, isolated, and purified prior to hydrogenation with additional reagents and/or catalysts. In the last years, a few examples of combined ROMP of cyclic olefins and subsequent hydrogenation without the need of isolation of the polymer from the first step or deactivation of the olefin metathesis catalyst have appeared in the patent literature. However, metathesis is carried out with a binary catalytic system (e.g., WCl_6/Sn^tBu_4) and then another catalyst must be added for hydrogenation [7]. Sunaga et al. have described a one-pot process of Mo-catalyzed ROMP, followed by homogeneous hydrogenation with $RuCl_2(PPh_3)_4$ under forcing conditions (165 °C, > 70 atm H_2) [6].

Several authors have developed tandem metathesis–hydrogenation processes using ruthenium carbene complexes of the Grubbs-type $RuCl_2(=CHR)(PR'_3)_2$ as catalysts [8–14]. For instance, McLain et al. have reported

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[*] Corresponding author.
E-mail address: maester@unizar.es (M.A. Esteruelas).

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the synthesis of an ethylene/methylacrylate copolymer by the ROMP of an ester-functionalized cyclooctene using $RuCl_2(=CHCH=CPh_2)(PCy_3)_2$, followed by the application of hydrogen pressure to the completed ROMP reaction at 135 °C. Under hydrogen pressure, the metathesis catalyst residue was assumed to be converted to $RuHCl(PCy_3)_2$. However, hydrogen pressures of at least 28 atm were required to maintain catalytic activity and achieve $> 99\%$ reduction [8]. An alternative procedure involving sequential homogeneous metathesis/heterogeneous hydrogenation has been developed by Wagener's group: Addition of silica gel to a completed homogeneous metathesis polymerization catalyzed by $RuCl_2(=CHPh)(PCy_3)_2$ generates a highly effective heterogeneous catalytic system that hydrogenates the unsaturated polymer under mild conditions (aprox. 8.5 atm) [9,10]. However, difficulties in separating the reduced polymer from the silica support limit the utility of this method to soluble polyolefins. Fogg and co-workers have recently described the tandem ROMP–hydrogenation of cyclooctene in the presence of $RuCl_2(=CHPh)(PCy_3)_2$ under exceptionally mild, homogeneous conditions (1 atm of H_2, 60 °C) when methanol and base are added after the metathesis process [11–13].

The five-coordinate hydride–chloro complex $OsHCl(CO)(P^iPr_3)_2$ is an active catalyst for the reduction of unsaturated organic substrates [15–20] and for the addition of silanes to alkynes [21]. Furthermore, we have observed recently that in the presence of diethylamine it also catalyzes alkyne-coupling reactions to afford butatrienes [22]. Now we have observed that $OsHCl(CO)(P^iPr_3)_2$ catalyzes not only the ring-opening metathesis polymerization of norbornene and 2,5-norbornadiene to afford poly(norbornene) and poly(norbornadiene), respectively, but also is an active catalyst in tandem ROMP–hydrogenation of both norbornene and 2,5-norbornadiene. The catalytic performance of the ruthenium counterpart, $RuHCl(CO)(P^iPr_3)_2$, in both reactions is also included.

2. Experimental

2.1. General considerations

All manipulations were carried out with rigorous exclusion of air using standard Schlenk techniques. Solvents were dried by known procedures and distilled under argon prior to use. $OsHCl(CO)(P^iPr_3)_2$ and $RuHCl(CO)(P^iPr_3)_2$ were prepared as previously reported [23]. Norbornene (Aldrich) was used as received. 2,5-Norbornadiene (Aldrich) was passed through an Al_2O_3 column prior to use. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded either on a Varian Gemini 2000 or on a Bruker AXR 300 instrument. Chemical shifts are referenced to residual solvent peaks. Gel-permeation chromatography (GPC) was carried out in a Waters liquid chromatography system equipped with a 600E multisolvent delivery system and 996 photodiode array detector. Two Ultrasyragel columns (Waters, pore size 500–104 Å) were connected in series. THF was used as the mobile phase with a flow rate of 0.8 mL min^{-1}. Calibration was performed with polystyrene standards. Thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC) were carried out heating the samples at 10 °C min^{-1} from 25 to 800 °C with a nitrogen (or helium) flow of 20 cm^3 min^{-1}. The second run has been performed heating the sample to 200 °C, cooling it to 25 °C, and then heating again from 25 to 800 °C. Samples (10 mg) were placed in a crucible, part of a Setaram TGDSC 111 instrument.

2.2. ROMP of norbornene catalyzed by $OsHCl(CO)(P^iPr_3)_2$

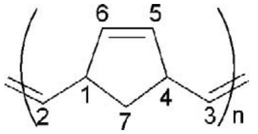
The amount of 13.8 mg (0.024 mmol) of $OsHCl(CO)(P^iPr_3)_2$ was dissolved in a solution of norbornene (226 mg, 2.4 mmol) in the chosen solvent (12 mL), and the resulting solution stirred at 40 °C. Depending on the solvent used, either a white polymer started to precipitate from the solution after 20 min or the solution became gradually more viscous. After stirring for 22 h at 40 °C, two different isolation methods were used:

(a) When alcohols were used as solvents, the solvent was removed and the white polymer washed repeatedly with the solvent, and dried under vacuum.
(b) When toluene or chlorobenzene were used as solvents the solution was poured into stirred methanol (20 mL). The precipitated polymer was recovered by centrifugation, washed several times with methanol, and dried under vacuum.

^1H NMR (300 MHz, $CDCl_3$, 20 °C): δ 5.20 (m, 2H, =CH), 2.78 (br s, 2H, CH), 1.86 (m, 3H, $–CH_2–$), 1.35 (br s, 2H, $–CH_2–$), 1.00 (m, 1H, $–CH_2–$). $^{13}C\{^1H\}$ NMR (75.43 MHz, $CDCl_3$, 20 °C): δ 133.8 (s, =CH), 42.7 (s, $–CH_2$), 38.6 (s, –CH), 33.2 (s, $–CH_2–$).

2.3. ROMP of 2,5-norbornadiene catalyzed by $OsHCl(CO)(P^iPr_3)_2$

To a solution of $OsHCl(CO)(P^iPr_3)_2$ (13.8 mg, 0.024 mmol) in 2-propanol (12 mL) was added 2,5-norbornadiene (260 µL, 2.4 mmol), and the resulting pale orange solution stirred at the set temperature (40 or 70 °C). As the reaction proceeds a white polymer precipitates from the solution. After 24 h the suspension was cooled to room temperature and then it was poured into stirred methanol. The precipitated polymer was recovered by centrifugation, washed with methanol (3×5 mL), and dried under vacuum for several hours at 40 °C. Yield: 40 °C, 57 mg (26%); 70 °C, 170 mg (76%). ^1H and $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) show that the formed polymer is *cis*-poly(norbornadiene). ^1H NMR (300 MHz, $CDCl_3$, 20 °C): δ 5.55 (s, 2H, $H^{5,6}$), 5.21 (m, 2H, $H^{2,3}$), 3.64 (m, 2H, $H^{1,4}$), 2.36 (m, 1H, $H^{7'}$), 1.22 (m, 1H, H^7). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 20 °C): δ 135.1 (s, $C^{5,6}$), 133.5 (s, $C^{2,3}$), 43.8 (s, $C^{1,4}$), 39.6 (s, C^7).



2.4. Hydrogenation of poly(norbornene) and poly(norbornadiene)

One hundred milligrams of polymer was dissolved, with heating, in 10 mL of xylene, followed by the addition of 500 mg of *p*-toluenesulfonylhydrazide. The mixture was stirred at 120 °C for 2.5 h and then it was filtered and the hot filtrate poured into methanol (30 mL). The precipitated polymer was recovered by centrifugation, washed several times with methanol, and dried under vacuum to yield the hydrogenated polymer. The hydrogenated polymer was characterized by NMR spectroscopy at 55 °C. ^1H NMR (300 MHz, $CDCl_3$, 55 °C): δ 1.90 (br, 2H), 1.72 (br, 4H), 1.28 (br, 4H), 1.15 (br, 2H). $^{13}C\{^1H\}$ NMR (75.429 MHz, $CDCl_3$, 55 °C): δ 40.7 (s, C^7), 40.4 (s, $C^{1,4}$), 35.7 (s, $C^{2,3}$), 31.7 (s, $C^{5,6}$) (see Fig. 2 for assignments).

2.5. Spectroscopic characterization of $OsHCl(CO)(\eta^2\text{-}C_7H_{10})(P^iPr_3)_2$

In a 5-mm NMR tube $OsHCl(CO)(P^iPr_3)_2$ (30 mg, 0.052 mmol) and norbornene (12.3 mg, 0.13 mmol) were dissolved in 0.4 mL of toluene-d_8, and the sample was cooled at −30 °C, changing the color of the solution from orange-reddish to colorless. ^1H and $^{31}P\{^1H\}$ NMR spectra recorded at this temperature show quantitative formation of the title compound. Upon heating at room temperature the orange-reddish color was recovered. ^1H NMR (300 MHz, toluene-d_8, −30 °C): δ 3.15 (t, $J_{H–H} = 3.3$, 2H, =CH), 2.99 (br, 2H, –CH), 2.60 (very br, 6H, $PCH(CH_3)_2$), 1.77 (br d, $J_{H–H} = 7.2$, 2H, $–CH_2–$), 1.98 (br, 36H, $PCH(CH_3)_2$), 0.75 (d, $J_{H–H} = 9.6$, 1H, bridging $–CH_2–$), three of the protons of the coordinated norbornene are overlapped by the $PCH(CH_3)_2$ resonance, −5.94 (t, $J_{P–H} = 27$, 1H, OsH). $^{31}P\{^1H\}$ NMR (121.4 MHz, toluene-d_8, −30 °C): δ 11.8 (s). $^{13}C\{^1H\}$ NMR (75.43, toluene-d_8, −30 °C, plus apt): δ 180.7 (t, $J_{P–C} = 8.7$, CO), 63.6 (s, =CH), 44.6 (s, –CH), 37.0 (s, bridging $–CH_2–$), 30.0 (s, $–CH_2–$), 20.7 (s, PCH-$(CH_3)_2$), 19.8 (br, $PCH(CH_3)_2$).

2.6. Tandem ROMP–hydrogenation of norbornene catalyzed by $OsHCl(CO)(P^iPr_3)_2$

In a Fischer–Porter bottle $OsHCl(CO)(P^iPr_3)_2$ (13.8 mg, 0.024 mmol) and norbornene (226 mg, 2.4 mmol) were dissolved either in 2-propanol or toluene (15 mL). As the ROMP reaction proceeds, a white polymer appears when 2-propanol is used, or in the case of toluene the viscosity of the solution increases. After stirring at 40 °C for 24 h, the argon atmosphere was replaced by hydrogen (3 atm), and it was stirred for 48 h at 40 °C. After this time two different isolation methods were used: When 2-propanol was used the polymer was filtered off, washed with methanol, and dried under vacuum for several hours. Yield: 215 mg (93%). When toluene was used, methanol (20 mL) was added and then a white polymer came off from the solution. This polymer was washed with methanol and dried under vacuum for several hours. Yield 164 mg (71%). These polymers were characterized by NMR spectroscopy at 55 °C. ^1H NMR (300 MHz, $CDCl_3$, 55 °C): δ 1.90 (br, 2H), 1.72 (br, 4H), 1.28 (br, 4H), 1.15 (br, 2H). $^{13}C\{^1H\}$ NMR (75.429 MHz, $CDCl_3$, 55 °C): δ 40.7 (s, C^7), 40.4 (s, $C^{1,4}$), 35.7 (s, $C^{2,3}$), 31.7 (s, $C^{5,6}$).

2.7. Tandem ROMP–hydrogenation of 2,5-norbornadiene catalyzed by $OsHCl(CO)(P^iPr_3)_2$

In a Fischer–Porter bottle $OsHCl(CO)(P^iPr_3)_2$ (25.9 mg, 0.045 mmol) was dissolved in 15 mL of 2-propanol and 2,5-norbornadiene (580 µL, 5.4 mmol) was added. The resulting pale orange solution was stirred under argon at 40 °C for 48 h, and during this time the solution color changed to pink and a white polymer precipitated. After this time the argon atmosphere was replaced by H_2 (3 atm). The white suspension was stirred at 75 °C for 24 h, and a decrease of the H_2 pressure was observed during this time. The bottle was refilled with H_2 (3 atm) and the suspension stirred for an additional 6 h at 40 °C. After this time, it was poured into stirred methanol (15 mL). The precipitated polymer was recovered by centrifugation, washed with methanol (3 × 5 mL), and dried under vacuum for several hours at 40 °C. Yield: 140 mg (27%). ^1H and $^{13}C\{^1H\}$ NMR spectra of the polymer recorded at 55 °C were identical to those obtained for the tandem ROMP–hydrogenation of norbornene.

2.8. Spectroscopic characterization of $OsHCl(CO)(\eta^2\text{-}H_2)(P^iPr_3)_2$

In a 5-mm NMR tube $OsHCl(CO)(P^iPr_3)_2$ (10 mg, 1.74×10^{-2} mmol) and norbornene (8.2 mg, 8.7×10^{-2} mmol) were dissolved in 0.4 mL of toluene-d_8. After 24 h the ^1H and $^{31}P\{^1H\}$ NMR spectra show peaks corresponding to $OsHCl(CO)(P^iPr_3)_2$ and to poly(norbornene). The argon atmosphere was replaced by H_2 (1 atm), and the NMR tube sealed and shaken. ^1H and $^{31}P\{^1H\}$ NMR spectra show immediate and quantitative formation of $OsHCl(CO)(\eta^2\text{-}H_2)(P^iPr_3)_2$. ^1H NMR (300 MHz, toluene-d_8, 20 °C): δ 2.50 (m, 6H, $PCH(CH_3)_2$), 1.21 (dvt, $J_{H–H} = 7.2$, $N = 13.8$, 36H, $PCH(CH_3)_2$)), −1.82 (br, 2H, $Os(\eta^2\text{-}H_2)$), −8.00 (very br, 1H, Os–H). $^{31}P\{^1H\}$ NMR (121.4 MHz, toluene-d_8, 20 °C): δ 36.3.

2.9. ROMP of norbornene catalyzed by RuHCl(CO)(P^iPr_3)$_2$

The amount of 11.66 mg (0.024 mmol) of RuHCl(CO)(P^iPr_3)$_2$ was dissolved in a solution of norbornene (226 mg, 2.4 mmol) in 2-propanol or toluene (12 mL), and the resulting solutions were stirred at 40 °C. In 2-propanol a white polymer started to precipitate from the solution after 20 min and in toluene the solution became gradually more viscous. After stirring for 24 h (2-propanol) or 6 h (toluene) at 40 °C the polymer was isolated using the same methodology described for the ROMP of norbornene catalyzed by OsHCl(CO)(P^iPr_3)$_2$. ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ 5.32 (m, 2H, =CH), 2.40 (br s, 2H, CH), 1.79 (m, 3H, –CH_2–), 1.33 (br s, 2H, –CH_2–), 1.03 (m, 1H, –CH_2–). $^{13}C\{^1H\}$ NMR (75.43 MHz, $CDCl_3$, 20 °C): δ 133.1 (s, =CH), 46.0 (s, –CH_2), 41.3 (s, –CH), 32.1 (s, –CH_2–).

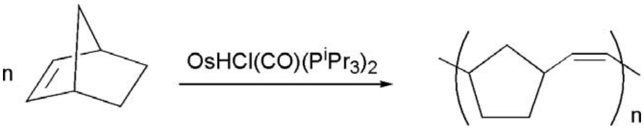
2.10. Tandem ROMP–hydrogenation of norbornene catalyzed by RuHCl(CO)(P^iPr_3)$_2$

In a Fischer–Porter bottle RuHCl(CO)(P^iPr_3)$_2$ (11.66 mg, 0.024 mmol) and norbornene (226 mg, 2.4 mmol) were dissolved either in 2-propanol or toluene (15 mL). As the ROMP reaction proceeds, a white polymer appears when 2-propanol is used, or in the case of toluene, the viscosity of the solution increases. After stirring at 40 °C for 24 h (2-propanol) or 7.5 h (toluene), the argon atmosphere was replaced by hydrogen (3 atm), and it was stirred for 48 h at 40 °C. After this time the polymer was isolated using the same methodology described for the tandem ROMP–hydrogenation of norbornene catalyzed by OsHCl(CO)(P^iPr_3)$_2$. Yield: 187 mg (81%, 2-propanol); 182 mg (79%, toluene). The polymers were characterized by NMR spectroscopy at 55 °C. The ^{1}H and $^{13}C\{^1H\}$ NMR spectra are identical to those recorded for the hydrogenated poly(norbornene) prepared using OsHCl(CO)(P^iPr_3)$_2$ as catalyst of the process.

3. Results and discussion

3.1. ROMP of norbornene and 2,5-norbornadiene catalyzed by OsHCl(CO)(P^iPr_3)$_2$

When the complex OsHCl(CO)(P^iPr_3)$_2$ was treated with 100 eq of norbornene, it was observed depending on the solvent used that either a white fibrous material precipitates from the solution (alcohols) or the viscosity of the solution increases with time. After isolation, a white material characterized as *cis*-poly(norbornene) was obtained in high yield.



(1)

The ROMP of norbornene catalyzed by OsHCl(CO)(P^iPr_3)$_2$ was examined in a variety of solvents. The results are summarized in Table 1. In general, alcohols lead to the best results, in terms of conversion. However, the solvent used for the polymerization reaction does not greatly affect the nature of the polymer formed. The polymerization does not proceed through a radical mechanism, since no change is observed when the process takes place in the presence of a radical inhibitor as hydroquinone or 2,6-di-*tert*-butyl-*p*-cresol (runs 5 and 7). The resulting polymers have been characterized by IR, ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopies, GPC, TGA, and DSC.

Infrared spectra of the poly(norbornene) show bands at 730 cm^{-1} (bending mode due to *cis* disubstituted C=C double bonds). Both ^{1}H and $^{13}C\{^1H\}$ NMR spectra are consistent, in all cases, with the predominant formation of *cis*-poly(norbornene) [24–26]. The ^{1}H NMR spectrum in chloroform-*d* shows a multiplet centered at 5.20 ppm, assigned to the olefinic *cis* protons, while the $^{13}C\{^1H\}$ NMR spectrum shows a singlet at 133.8 assigned to the carbon atoms of the double bonds of the polymer.

Number average molecular weight (M_n) and weight average molecular weight (M_w) determinations by GPC range

Table 1
Polymerization of norbornene catalyzed by OsHCl(CO)(P^iPr_3)$_2$[a]

Run	Temperature (°C)	Solvent	S/C	Time (h)	Yield (%)	M_n	M_w	M_w/M_n	σ_c
1	70	Benzene-d_6	113	0.67	100[b]	11,400	32,000	2.80	0.74
2	70	Toluene	100	1	49.7	48,500	65,600	1.35	0.95
3	40	Toluene	100	23	80	95,800	132,500	1.38	0.94
4	40	^iPrOH	100	23	100	117,300	254,000	2.16	0.95
5[c]	40	^iPrOH	100	23	100	140,400	457,900	3.36	0.95
6	40	C_6H_5Cl	100	22	61	167,800	198,000	1.18	0.77
7[c]	40	C_6H_5Cl	100	23	73	211,800	228,500	1.08	0.95
8	40	^nPrOH	100	23	98	35,000	70,200	2.00	0.92
9	40	^tBuOH	100	23	31	215,300	486,600	2.26	0.87
10	40	^nBuOH	100	23	98	62,500	96,500	1.54	0.95
11	40	Acetone	100	23	26	309,000	428,000	1.38	0.85

[a] S/C: ratio norbornene/catalyst; σ_c is the fraction of cis double bonds.

[b] The reaction was carried out in an NMR tube.

[c] In the presence of hydroquinone.

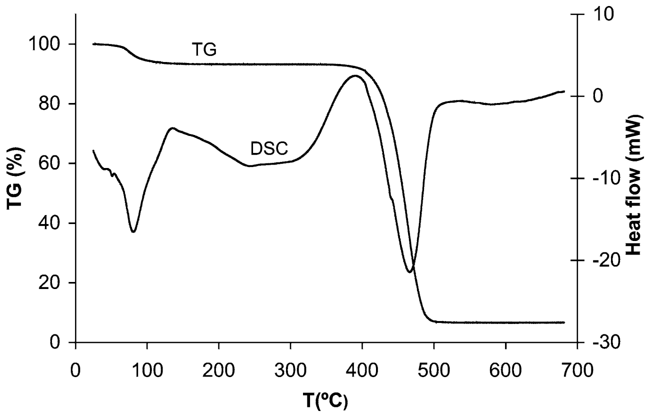


Fig. 1. TGA and DSC curves for *cis*-poly(norbornene) prepared in 2-propanol using OsHCl(CO)(P^{i}Pr$_3$)$_2$ as catalyst.

from 11,400 to 309,000 (M_n) and from 32,000 to 486,600 (M_w). In all cases, monomodal distributions with polydispersity indexes between 1.1 and 3.4 were found.

Fig. 1 shows typical TGA and DSC curves for *cis*-poly(norbornene) obtained in 2-propanol. The TGA curve reveals a slight weight loss (less than 5%) at 85 °C associated to the loss of the solvent soaked up by the polymer. In agreement with this, the DSC curve contains an endothermic peak, which shows a shoulder between 30 and 40 °C. This feature could be due to a glass transition (T_g) of the polymer. Between 150 and 350 °C, the TGA curve does not suggest changes in the material. However, the DSC curve indicates that there is a somewhat broad heat absorption, due to the melting of the polymer. Different *cis*-poly(norbornene) samples, that differ in the solvent used for the ROMP reaction, exhibited analogous DSC curves with slight differences in the melting temperature range and in the melting enthalpy. Near 460 °C the decomposition of the polymer takes place (466 °C, minimum DTG). Thus, the DSC curve shows a strong heat adsorption that, according to the TGA curve, is associated to ca. 97% weight loss. The decomposition temperature of the *cis*-poly(norbornene)s prepared in other solvents is very close to this temperature. In some cases we observe a small shoulder at 441 °C, which could be due to the small fraction of *trans*-poly(norbornene) present in the samples.

With the exception of OsCl$_3$ [27–41], only a few osmium derivatives have been reported to be active precursors for the ROMP of norbornene. The complex (*p*-cymene)OsCl$_2$(PCy$_3$) is an active catalyst for this reaction after activation by ultraviolet light. However, no data about selectivity were reported [42]. Compounds Cp$_2^*$Os$_2$Br$_4$, Cp*Os(COD)Br, and H$_2$OsBr$_6$ have been found active catalysts in ROMP of norbornene, and the formed polymer has a *cis* content ranging from 58 to 73% [43]. It has also been observed that the reactivity of these compounds is greatly enhanced when they are activated with the stoichiometric amount of AlMe$_3$ or methylaluminoxane (MAO) [43]. Aimé and co-workers have reported recently the ROMP activity of an osmium cluster, Os$_3$(μ-H)$_2$(CO)$_{10}$. Initially, the poly(norbornene) formed has a *cis* stereochemistry, but after 5 days the *trans* isomer is predominantly obtained (ratio *trans*/*cis* 12/1) [44]. The ROMP of norbornene catalyzed by OsO$_4$ has been also studied, getting 5% of poly(norbornene) after 3 days at 60 °C. The formed poly(norbornene) has a 75–80% *cis* content [45].

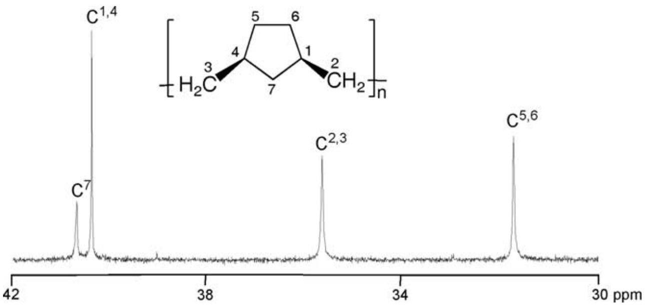
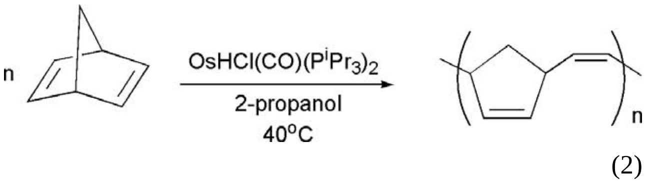


Fig. 2. ^{13}C{^{1}H} NMR spectrum (CDCl$_3$, 55 °C, 75.4 MHz) of hydrogenated poly(norbornene).

The most notable feature of the ROMP of norbornene catalyzed by OsHCl(CO)(P^{i}Pr$_3$)$_2$ is the high stereoselectivity of the reaction. In most of the runs, the fraction of *cis* double bonds (σ_c) is 0.95. This value is only comparable to that obtained using OsCl$_3$, and the system formed by treatment of OsCl$_3$ with PhC≡CH as catalysts. They afford poly(norbornene)s whose σ_c values are 0.93 and 0.98, respectively, [38].

When poly(norbornene)s are high *cis* (or high *trans*), their hydrogenated derivatives can be used to determine the tacticity. So, in order to determine the stereoregularity of the poly(norbornene), we have carried out the hydrogenation of the double bonds using diimine generated in situ from *p*-toluenesulfonylhydrazide [46]. The fully hydrogenated polymer was moderately soluble in chloroform-*d* at 55 °C and, as a result, the ^{13}C{^{1}H} NMR spectrum could be recorded (Fig. 2). The lines sensitive to tacticity, C^7 and C^{5,6}, appear as singlets. This indicates that the polymer is not atactic. The distinction between syndiotactic and isotactic poly(norbornene) has been made preparing hydrogenated syndiotactic poly(norbornene) using OsCl$_3$/phenylacetylene as catalyst [38], and recording its ^{13}C{^{1}H} NMR spectrum in chloroform-*d* at 55 °C. The comparison between this spectrum and those of our hydrogenated poly(norbornene) allows us to conclude that the poly(norbornene) formed using OsHCl(CO)(P^{i}Pr$_3$)$_2$ as catalyst is syndiotactic, since the chemical shifts are the same.

The complex OsHCl(CO)(P^{i}Pr$_3$)$_2$ is also active in the ROMP of 2,5-norbornadiene. The process has been performed in 2-propanol, under similar conditions to those described for norbornene. The reaction leads to poly(norbornadiene) in 27% yield.



(2)

When the reaction is carried out at 70 °C the yield increases up to 76%. The white material has been characterized by ^{1}H and ^{13}C{^{1}H} NMR in chloroform-*d* as *cis*-poly(norbornadiene) ($\sigma_c = 0.95$). Unfortunately, the molecular weight could not be determined due to the poor solubility of the polymer in tetrahydrofuran at room temperature.

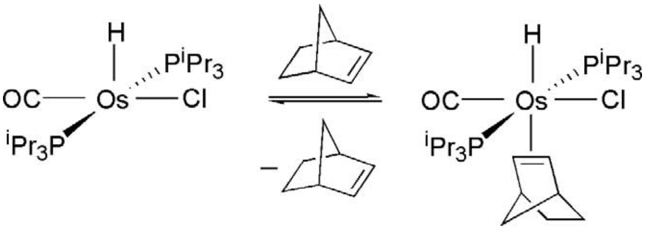
The previous studies of ROMP of 2,5-norbornadiene catalyzed by osmium compounds have been limited to $OsCl_3$. The resulting poly(norbornadiene) is highly *cis* ($\sigma_c = 0.90$) [38,40,41,47].

Hydrogenation of the poly(norbornadiene) using diimine generated in situ from *p*-toluenesulfonylhydrazide leads to a saturated polymer. The ^{1}H and ^{13}C{^{1}H} NMR spectra in chloroform-*d* at 55 °C are identical to those obtained from poly(norbornene). This indicates that the polymer is syndiotactic.

3.2. Mechanism

As noted previously, the polymerization does not proceed through a radical mechanism, since no change was observed in the presence of a radical inhibitor. Furthermore, the monomodal weight distribution suggests that only one mechanism is involved in the catalysis. In order to obtain information about it, we have investigated the spectroscopic features of a mixture of $OsHCl(CO)(P^iPr_3)_2$ and norbornene.

The ^{1}H NMR spectrum at room temperature of a solution in toluene-d_8 of $OsHCl(CO)(P^iPr_3)_2$ and 5 eq of norbornene shows, initially, a slight broadening of the hydride resonance of the osmium complex, whereas in the ^{31}P{^{1}H} NMR spectrum a very broad resonance at 49 ppm is observed. The broadness of the hydride resonance, as well as the broadening observed in that of the ^{31}P{^{1}H} NMR spectrum, suggests that in solution complex $OsHCl(CO)(P^iPr_3)_2$ is in rapid equilibrium with a six-coordinate species containing a coordinated molecule of norbornene.

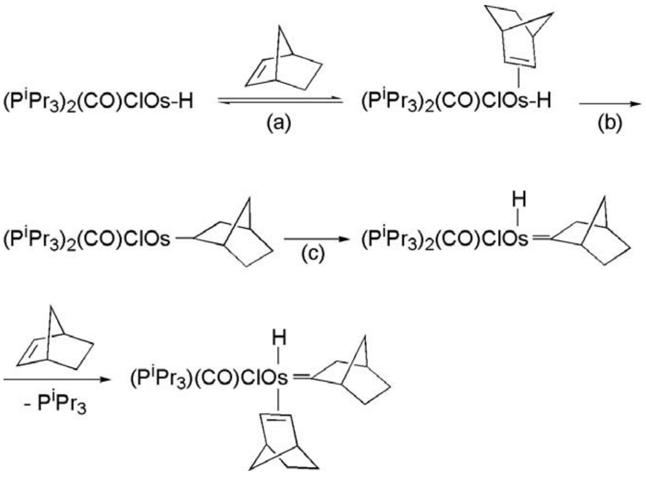


(3)

According to this, when the sample was cooled at −30 °C the formation of a new species, characterized as $OsHCl(CO)(\eta^2\text{-}C_7H_{10})(P^iPr_3)_2$, was observed. The most noticeable feature in the ^{1}H NMR spectrum of this compound is a triplet at −5.94 ppm with an H–P coupling constant of 27 Hz, assigned to the hydride resonance. This chemical shift agrees well with those previously reported for related $OsHX(CO)(\eta^2\text{-olefin})(P^iPr_3)_2$ complexes (X = Cl, OH), where the mutually *trans* disposition of the olefin and the hydride ligands has been structurally proven [23,48,49]. The coordination of norbornene is reflected in the chemical shifts of the olefinic protons, which move from 5.97 ppm in free norbornene to 3.15 ppm in $OsHCl(CO)(\eta^2\text{-}C_7H_{10})(P^iPr_3)_2$. A similar shift toward a higher field has been observed for the olefin resonances in the related osmium–η^2-olefin complexes [23,48,49]. The ^{13}C{^{1}H} NMR spectrum also supports the coordination of the norbornene to the osmium atom. Thus, the olefinic resonance is observed at 63.6 ppm, shifted 72 ppm toward a higher field with regard to that of free norbornene.

The spectra of the catalytic solution at room temperature in toluene-d_8 show no further signals apart from those of $OsHCl(CO)(P^iPr_3)_2$, norbornene, and the forming poly(norbornene). This indicates that the concentration of the active species is too low to be detected by NMR spectroscopy. We assume that the required species for ROMP of norbornene is an osmium–carbene generated in situ. This carbene intermediate could be formed via insertion of the coordinated norbornene into the Os–H bond of $OsHCl(CO)(\eta^2\text{-}C_7H_{10})(P^iPr_3)_2$, to form the norbornyl derivative shown in Scheme 1 (step b). Although alkyl products resulting from the insertion of olefins into the Os–H bond have not been detected, the existence of a rapid equilibrium between the hydride–olefin and alkyl species in these type of systems has been proven [18,50]. The insertion should be followed by an α-elimination reaction on the norbornyl ligand (step c) to give an hydride–carbene intermediate. In this context, it should be noted that complexes of formula $OsHCl({=}CR_2)(CO)(PR'_3)_2)$ ($R'_3 = {}^iPr_3, {}^tBu_2Me$) are known [49,51].

Once the hydride–carbene intermediate is formed, a second molecule of olefin should enter in the coordination sphere of the osmium center. Since this hydride–carbene intermediate is saturated, either decoordination of the chlorine atom (to give a cationic species) or decoordination of one of the phosphine ligands should occur. In favor of the second process we have found that the polymerization is completely inhibited by addition of three equivalents of P^iPr_3 per equivalent of catalyst, while the reaction proceeds when



Scheme 1.

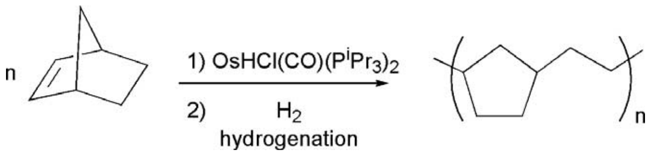
it is carried out in 2-propanol and in the presence of three equivalents of NaCl per equivalent of catalyst. Once the second molecule of olefin coordinates to the osmium center, the polymerization follows the typical growing chain involving the metallacyclization and cycloreversion steps [52].

Transition metal–hydride complexes have been proposed as responsible for ROMP and dimerization of norbornene when these reactions are catalyzed by several transition metal halides [53–56].

3.3. *Tandem ROMP–hydrogenation of norbornene and 2,5-norbornadiene catalyzed by OsHCl(CO)(P^{i}Pr$_3$)$_2$*

The complex OsHCl(CO)(P^{i}Pr$_3$)$_2$ has a very rich catalytic chemistry. Among the catalytic reactions promoted by this derivative is olefin hydrogenation [15–20]. We now show that it is also active in ROMP of norbornene and 2,5-norbornadiene. These results prompted us to combine both processes, in the search for a tandem catalytic process of metathesis–hydrogenation based on osmium, which was unknown until now.

The tandem ROMP–hydrogenation processes of norbornene catalyzed by OsHCl(CO)(P^{i}Pr$_3$)$_2$ have been carried out at mild temperature (40 °C), either in toluene or in 2-propanol. In a typical experiment, norbornene and OsHCl(CO)(P^{i}Pr$_3$)$_2$ in a molar ratio 100/1 were dissolved in the chosen solvent and stirred under an argon atmosphere for 24 h. After this time, the argon atmosphere was replaced by H_2 (3 atm) and stirred for 48 h. As a result of this procedure, white materials in 93% (2-propanol) or 71% (toluene) yield were isolated and characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopies in chloroform-*d* at 55 °C as hydrogenated syndiotactic poly(norbornene).



(4)

The molecular weight could not be determined due to the poor solubility of the polymer in tetrahydrofuran at room temperature. The polymer melts at 139 °C, and no T_g is observed, in agreement with the thermal properties of hydrogenated poly(norbornene) previously reported [57].

We have also studied the tandem ROMP–hydrogenation of 2,5-norbornadiene catalyzed by OsHCl(CO)(P^{i}Pr$_3$)$_2$. Under the same conditions as those employed for norbornene (i.e., 40 °C, 3 atm H_2), the polymer is not hydrogenated. However, when the temperature is raised to 75 °C, it is fully hydrogenated. The ^{13}C{^{1}H} NMR spectrum of the hydrogenated material is identical to that of hydrogenated poly(norbornene). This indicates that both endocyclic and exocyclic carbon–carbon double bonds of poly(norbornadiene) have been hydrogenated.

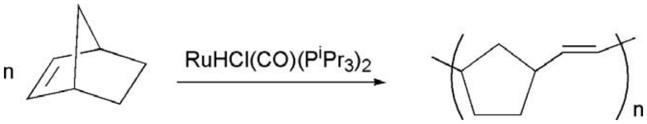
It should be noted that this finding represents the first report on a tandem ROMP–hydrogenation process catalyzed by an osmium compound, and also that the conditions used to achieve the hydrogenation of the polymers are very mild.

In order to determine the nature of the osmium complex present in the solution during the hydrogenation step of the tandem process the following experiment was carried out: Complex OsHCl(CO)(P^{i}Pr$_3$)$_2$ was mixed with 5 eq of norbornene in an NMR tube, and they were dissolved in toluene-d_8 [58]. After 24 h all the norbornene was consumed and the ^{1}H NMR spectrum showed peaks assigned to poly(norbornene), along with those of OsHCl(CO)(P^{i}Pr$_3$)$_2$. The argon atmosphere was then replaced by H_2, and the color of the viscous solution changed immediately from orange to pale yellow. ^{1}H and ^{31}P{^{1}H} NMR spectra show quantitative formation of OsHCl(η^2-H$_2$)(CO)(P^{i}Pr$_3$)$_2$ [15, 18,59]. This complex was found to play a fundamental role in the rate-determining step of the catalytic reaction of hydrogenation of benzylideneacetone to 4-phenylbutan-2-one [19]. A catalytic cycle similar to that proposed for the reduction of this ketone can be also proposed for the hydrogenation of poly(norbornene) and poly(norbornadiene).

3.4. *ROMP and tandem ROMP–hydrogenation of norbornene catalyzed by RuHCl(CO)(P^{i}Pr$_3$)$_2$*

The results obtained with OsHCl(CO)(P^{i}Pr$_3$)$_2$ prompted us to test the catalytic ability of the ruthenium counterpart RuHCl(CO)(P^{i}Pr$_3$)$_2$ in ROMP of norbornene and 2,5-norbornadiene and tandem ROMP–hydrogenation of norbornene.

This complex was found to be active in the ROMP of norbornene in 2-propanol and toluene under similar conditions to those used for OsHCl(CO)(P^{i}Pr$_3$)$_2$,



(5)

while 2,5-norbornadiene yields a white material after 24 h, in 16% yield. Its low solubility prevents characterization. The results for norbornene are summarized in Table 2. As in the reactions catalyzed by OsHCl(CO)(P^{i}Pr$_3$)$_2$, the polymerization does not proceed through a radical mechanism, since no significant change is observed when the reaction is carried out in the presence of hydroquinone (run 3). The resulting polymers have been characterized as *trans*-poly(norbornene) by IR, and ^{1}H and ^{13}C{^{1}H} NMR spectroscopies, GPC, TGA, and DSC.

Infrared spectra of the poly(norbornene) show bands at 960 cm^{-1} (bending mode due to trans disubstituted C=C double bonds). Both ^{1}H and ^{13}C{^{1}H} NMR spectra agree with the predominant formation of *trans*-poly(norbornene) [24–26]. The ^{1}H NMR spectrum in chloroform-*d* shows a multiplet centered at 5.32 ppm, assigned to the olefinic *trans* protons, whereas the ^{13}C{^{1}H} NMR spectrum shows a singlet at 133.1 assigned to the carbon atoms of the double bonds of the polymer.

Table 2
Polymerization of norbornene catalyzed by $RuHCl(CO)(P^iPr_3)_2$[a]

Run	Solvent	time (h)	Yield (%)	M_n	M_w	M_w/M_n	σ_c
1	Toluene	6	90	24,400	120,800	4.95	0.12
2	2-Propanol	23	77	16,800	68,300	4.06	0.26
3[b]	2-Propanol	23	80	47,000	162,300	3.45	0.26

[a] The reactions were carried out at 40 °C, and the ratio norbornene/catalyst used was 100/1, σ_c is the fraction of cis double bonds.

[b] In the presence of hydroquinone.

It should be noted the different stereochemistry of the polymer obtained with the ruthenium and osmium catalysts. While complex $RuHCl(CO)(P^iPr_3)_2$ selectively affords *trans*-poly(norbornene), complex $OsHCl(CO)(P^iPr_3)_2$ gives predominantly *cis*-poly(norbornene). The different behavior between these complexes can be attributed, like in $RuCl_3$ and $OsCl_3$, to a substantial increase in ligand field effects and to the importance of the polar factor, when the ligands are the same, by changing the metal in the groups from the 4d to the 5d row [60,61].

Number average molecular weight (M_n) and weight average molecular weight (M_w) determinations by GPC range from 16,800 to 47,000 (M_n) and from 68,300 to 162,300 (M_w). In all cases monomodal distributions with polydispersity indexes between 4.06 and 4.95 were found.

Fig. 3 (top) shows the DSC and TGA for *trans*-poly(norbornene). The DSC curve shows a shoulder at ca. 30 °C, that could be due to the glass transition of the polymer. At about 90 °C an exothermic peak appears, which is associated with a slight weight increase (1–2%) in the TGA curve. A similar weight gain (2%) has been reported by Brumaghim and Girolami [43]. Between 90 and 350 °C a heat absorption without mass loss occurs. It is due to softening of the sample. A melting point is not observed and decomposition takes place at 457 °C (peak minimum of the heat flow). This value is ca. 10 °C lower than that of *cis*-poly(norbornene).

Several experiments were performed in order to explain the origin of the exothermic peak and gain weight:

(i) The sample was preheated to 200 °C, cooled, and then heated. As a result, neither the exothermic peak nor the weight gain are observed (Fig. 3 (bottom)). This indicates that they are not reversible.
(ii) The TGA-DSC was registered under both helium and nitrogen, and the same behavior was observed.
(iii) The TGA-DSC was registered in two different thermobalances, whose crucible have different surfaces exposed, and it was observed that the weight gain depends on the surface exposed.

The results of these experiments suggest that the exothermic peak and weight increase are due to the sorption of helium or nitrogen in the cavities of the polymer. The capability of poly(norbornene)s for packaging and gas separation has been proven [62,63].

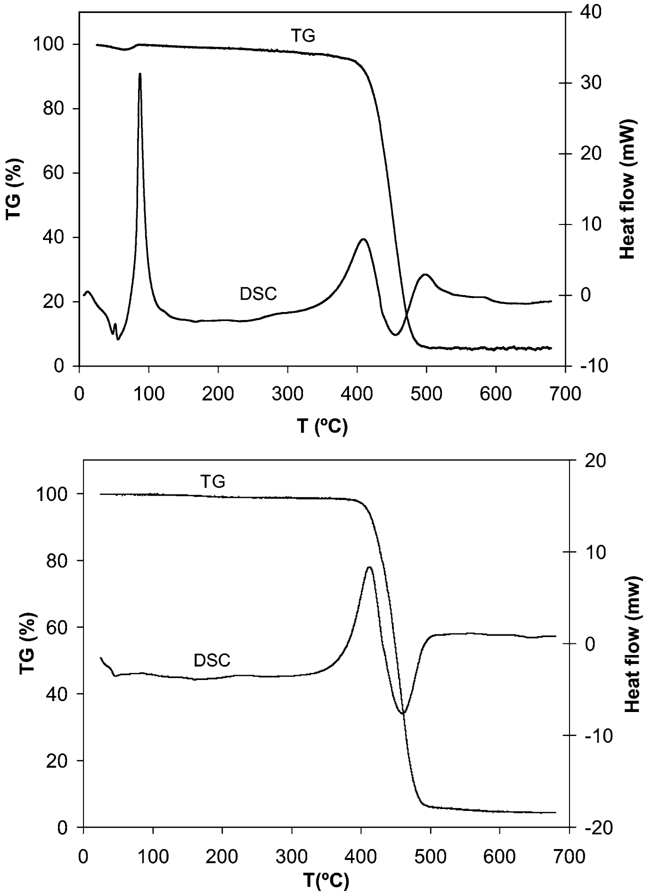


Fig. 3. (Top) TGA and DSC curves for *trans*-poly(norbornene) prepared in 2-propanol using $RuHCl(CO)(P^iPr_3)_2$ as catalyst. (Bottom) TGA and DSC curves for *trans*-poly(norbornene) preheated to 200 °C.

The complex $RuHCl(CO)(P^iPr_3)_2$ has been found to be also active in the tandem ROMP–hydrogenation of norbornene. The experiments have been performed at 40 °C either in toluene or in 2-propanol. In both cases, after 7.5 (toluene) or 24 h (2-propanol) the argon atmosphere was replaced by hydrogen (3 atm) and kept under H_2 for 48 h. As a result, white materials in about 80% yield were isolated and characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopies as hydrogenated poly(norbornene). From the $^{13}C\{^1H\}$ NMR spectra we deduced that the poly(norbornene) formed was syndiotactic.

4. Conclusion

The complex $OsHCl(CO)(P^iPr_3)_2$ catalyzes the ROMP of norbornene and 2,5-norbornadiene to give *cis*-syndiotactic poly(norbornene) and poly(norbornadiene), respectively. This complex also achieves the tandem ROMP–hydrogenation of both olefins under very mild conditions and represents the first report of the use of an osmium-based catalyst in such type of tandem reaction. The complex $RuHCl(CO)(P^iPr_3)_2$ is also active in ROMP and tandem–ROMP of norbornene and, in contrast to the osmium counterpart, *trans*-poly(norbornene) is obtained in the ROMP process.

Acknowledgments

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