meso-[Norbornane-7,7-bis(indenyl)]titanium Dichloride: A Highly Active Catalyst for Ethylene−Styrene Copolymerization

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ABSTRACT: The synthesis of the highly stereorigid *meso*-[norbornane-7,7-bis(indenyl)]titanium dichloride (*meso*-**1**) is described. The stereorigidity of this new *ansa*-metallocene is due to the inclusion of the norbornane skeleton as the bridge, since H-*exo* of norbornane hinders the rotation of the C7-indenyl bonds. *meso*-**1** shows very high activity in ethylene−styrene copolymerizations, yielding copolymers with unprecedented homogeneous chemical compositions. In addition, UHMWPE is obtained when a mixture of *rac*-**1**:*meso*-**1** (2.8:1) is used as catalyst in ethylene homopolymerization reactions.

Introduction

The design of new catalysts with enhanced catalytic properties remains a challenge in polymer science mainly due to the increasing need by the industry to obtain materials with modified properties (chemical, physical, mechanical, and electronic), ease of processability, compatibility with several additives and low cost.[1,2] A wider scope of different polymers can be prepared in copolymerization reactions and, therefore, the development of catalysts capable of copolymerizing two different monomers is highly desirable.

A large number of catalysts, such as conventional heterogeneous Ziegler−Natta catalysts, fail to obtain copolymers and normally induce homopolymerization of each of the monomers or a very low incorporation of the comonomer, due to the different reactivity shown by the monomers. The efficient copolymerization of ethylene with styrene became possible only with the use of metallocene catalysts. Cp′TiX3, which are very active styrene homopolymerization catalysts, show low activity in ethylene homopolymerization or ethylene−styrene copolymerization.[3] However, constrained geometry catalysts (CGC), in which an alkylimido ligand is introduced, are very active in the copolymerization of ethylene with a variety of comonomers, including styrene.[4,5] The first example of ethylene−styrene copolymerization using this type of half-sandwich metallocenes [Cp*SiMe$_2$(N-*t*-Bu)]TiCl$_2$ was reported by Dow company.[6] The reason for the high activity of CGC lies in the constrained, more open and less sterically hindered reactive center as well as the weaker π-donating character of the amido group.[7] The introduction of different substituents in the Cp ring and the amido group modifies the incorporation of styrene during the copolymerization.[8] This is very important since modifying the styrene content in the copolymer, materials with different properties can be obtained.[3b,8c,9−11] Very recently, the first example of efficient living copolymerization of ethylene−styrene catalyzed by (cyclopentadienyl)(ketimide)titanium(IV) complex-MAO catalyst system has been reported.[12] In this work we describe the synthesis of a new *ansa*-metallocene catalyst derived from norbornane and the study of its catalytic activity in ethylene−styrene copolymerization. We also report the analysis of some molecular details of the materials obtained.

Results and Discussion

In recent years, we have focused our attention on the homo- and copolymerization and properties of ethylene with different comonomers, both from experimental and computational points of view.[13] We have carried out the copolymerizations employing *ansa*-metallocenes as well as CGC. As expected, a higher activity was found using geometry constrained [Cp*SiMe$_2$(N-*t*-Bu)]TiCl$_2$ Dow catalyst. When *rac*-Et(H$_4$Ind)$_2$MCl$_2$ (M = Ti, Zr) were used, a very low activity, even for ethylene homopolymerization, was observed for the titanium system, while the zirconium system achieved monomer polymerization, incorporating small amounts of styrene. Our density functional computations show a good agreement between the experimental and computational results.[13]

In the present paper we have used a new *ansa*-metallocene catalyst derived from the rigid bicyclic system norbornane. When aryl substituents are introduced in position 7 of norbornane, the mobility of these groups is sterically hindered by the *exo*-hydrogens of the bicyclo. As a result, 7,7-diarylnorbornanes show high conformational stability, with a barrier to rotation of phenyl groups, in the case of 7,7-diphenylnorbornane (DPN), of 12.5 kcal/mol.[14] Consequently, unlike other diphenylmethane derivatives, the most stable conformation in DPN and derivatives is the cofacial gable disposition. Therefore, DPN's show two important characteristics that makes these compounds different: preorganization and aromatic homoconjugation between the aryl groups.[14] In previous works we have shown that these features can be the basis for the design of molecular clocks, homoconjugated polymers and chromophores with NLO properties as well as model compounds for the study of aromatic face-to-face and edge-to-face interactions.[15] We have now used 7,7-disubstituted norbornane to obtain a new *ansa*-metallocene catalyst, *meso*-[norbornane-7,7-bis(indenyl)]titanium dichloride (**1**) and tested its activity in ethylene−styrene copolymerization. It is well-known that small variations in the structure of the bridge in stereorigid ansa-metallocenes are able to affect significantly the catalytic activity of these compounds.[16−18] Therefore, it is expected that the introduction of norbornane

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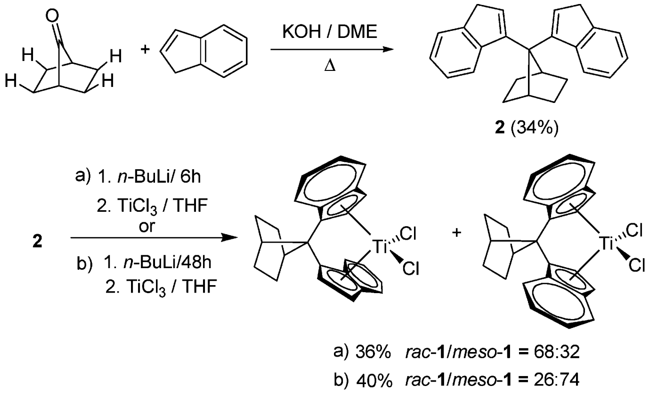
Scheme 1. Synthesis of *rac*- and *meso*-1



skeleton as the bridge in *ansa*-metallocene catalysts should increase the conformational stability of the ligands, fixing the geometry of the reactive site all along the catalytic process and influencing the reactivity of the catalyst.

The synthesis of **1** is described in Scheme 1. The reaction of 7-norbornanone[19] with indene/KOH following the procedure described in the literature[20] afforded the corresponding 7,7-bisindenylnorbornane (**2**) in moderate yield (34%). *ansa*-Metallocene **1** was obtained in 40% yield as a mixture of *rac/meso* isomers (26/74) according to the procedure described by Halterman.[21] Controlling the reaction conditions it is possible to obtain mixtures enriched in the *rac*- or *meso*-isomer. *meso*-**1** was separated and purified by recrystallization from toluene.

To gain information about the conformational stability of **1**, we determined the librational barrier of the indenyl group in the case of ligand **2** by DNMR, studying the coalescence of the methylenic indenyl protons. A value of 14.5 kcal/mol was obtained, which is ca. 2 kcal/mol higher than the librational barrier of the aryl rings in 7,7-diphenylnorbornane.[14,15d,22] Therefore, the high norbornane−indenyl rotational barrier is the main differential characteristic of ligand **2** which, as a consequence, shows a remarkable conformational stability, since small variations in the torsional angle C1Nor−C7Nor−C1Ind−C2Ind lead to considerable increases in the energies of the corresponding conformations due to steric hindrance with the *exo*-H of norbornane. It is then to be expected that metallocenes derived from ligand **2** should have a high restricted rotation of the norbornane−indenyl bonds. The effect of this characteristic is the fixing of the reactive center geometry during polymerization reactions.

We have carried out ethylene−styrene copolymerizations with **1** activated by MAO at several monomer-feeding ratios. The results are summarized in Table 1. Data of copolymerizations with CGC are also included in Table 1 for comparison. The copolymerizations have been carried out using both toluene and *n*-heptane as solvents but we obtained higher activities in toluene, while styrene contents were comparable. Therefore, only reactions in toluene are included in Table 1.

As expected, the styrene content in the polymers increases with the concentration of styrene in the reaction conditions in all cases, but the incorporation of styrene is slightly higher when CGC is used as catalyst (entries 2, 9, and 16 or 5, 12, and 17, Table 1).

We have compared the catalytic properties of *meso*-**1**, *rac*-**1**, and a mixture *rac*-**1**:*meso*-**1** = 2.8:1. As can be seen, *meso*-**1** shows higher activity, styrene content and yield than *rac*-**1** or mixtures of both isomers, being the differences in activity especially remarkable. In contrast, comparison of molecular weights and polidispersity index do not lead to a clear conclusion. The reason for the different behavior of the *meso*-isomer is actually under investigation.

Table 1. Ethylene/Styrene Copolymerizations Data[a]

entry	catalyst	[styrene][b]	yield[c]	activity[d]	styrene content[e]	M_w[f]	M_w/M_n
1	*meso*-**1**	0.00	14.00	24 138	0.0	560	1.7
2		0.33	16.06	11 727	1.4	560	2.3
3		0.76	12.74	5138	2.5	560	2.4
4		0.76	10.24	4251	2.9	340	2.0
5		1.29	11.86	2998	4.1	325	1.9
6	*rac*-**1**	0.00	9.59	16 534	0.0	790	8.3
7		0.76	1.75	1038	3.6	n.d.[h]	n.d.[h]
8	*rac*-**1**: *meso*-**1** (2,8:1)	0.00	9.72	9975	0.0	2300	2.5
9		0.33	4.06	740	1.0	610	2.9
10		0.33	3.40	621	1.7	660	2.6
11		0.76	3.56	359	2.4	395	2.0
12		1.28	4.92	313	3.5	450	2.1
13	CGC[g]	0.00	8.84	2540	0.0	273	2.6
14		0.06	8.44	1941	0.4	212	2.2
15		0.20	5.38	859	0.9	173	2.1
16		0.33	9.11	1108	2.2	170	2.2
17		1.29	10.75	445	5.3	164	2.3

[a] Polymerization conditions: toluene = 400 mL, [cat] = 20 μmol/L, Al:Ti = 2000, P(ethylene) = 3 bar, $T = 35$ °C. Key: entries 1−6, $t = 0.25$ h; entry 7, $t = 0.17$ h; entry 8, $t = 0.42$ h; entries 9−12, $t = 1$ h; entries 13−17, $t = 1.5$ h. [b] Styrene concentration in the feed in mol/L. [c] Units are given in g. [d] Monomer concentration is total olefin concentration (ethylene + styrene). Units are given in kg of polymer/[mol of Ti·h·(mol/L)$_{mon}$]. [e] Styrene content in mol % in the copolymer determined by ^{13}C NMR.[10] [f] Molecular weights in kg/mol were determined by gel permeation chromatography (GPC). [g] Referenced data.[13d] [h] n.d. = not determined.

The most important results of this work arise upon the comparison of the catalytic properties of *meso*-**1** and CGC (Dow) catalyst (entries 2/16 and 5/17, Table 1). As can be seen, *meso*-**1** shows a very high activity in ethylene−styrene copolymerization, 6.7−10.6 times higher than the activity of CGC. Also the yields and molecular weights are higher, while styrene content is slightly lower in the case of *meso*-**1**. The activity of *meso*-**1** is also considerably higher than the observed in other *ansa*-titanocenes and *ansa*-zirconocenes studied by us previously,[13c] a result that seems to indicate that the activity of these catalysts is controlled mainly by geometrical factors and not by the nature of the central metal atom. Finally, it should be pointed out that *meso*-**1** also shows a higher activity than CGC in ethylene homopolymerization reactions (entries 1 and 13, Table 1).

A very interesting result is obtained for the homopolymer (entry 8) synthesized from the mixture of isomers *rac*-**1**:*meso*-**1** (2.8:1). In this case, a very high molecular weight polymer (higher than 10^6 g·mol^{-1}) is obtained. This is an ultrahigh molecular weight polyethylene (UHMWPE), which is especially interesting for specific applications. Indeed, UHMWPE has a unique combination of properties for its use under the strongest wear and environmental conditions. In fact, this polymer is known as the thermoplastic material with both highest impact strength and resistance to abrasion. This combination of properties makes UHMWPE an exceptional material for industrial applications and for its use as a wear face in orthopedic implants in joint replacements.[23]

The development of (metallocene) single-site catalysts has made possible the examination of the relationship between the microstructure and the physical and chemical properties of polyolefins since these catalyst systems are able to produce materials with homogeneous chemical composition distributions (CCD). In this context, crystallization analysis fractionation (CRYSTAF) is a powerful methodology to resolve the chemical composition of polymeric samples.[24] The CRYSTAF profiles of the samples obtained by norbornane−indenyl catalyst system

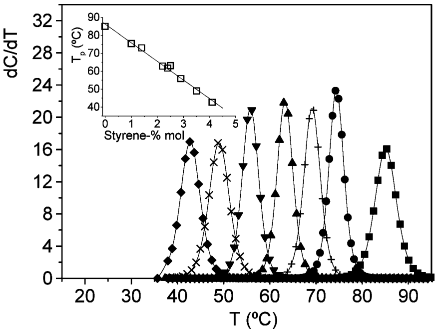


Figure 1. CRYSTAF profiles of poly(ethylene-*co*-styrene) samples obtained from the norbornane–indenyl catalyst systems exhibiting a range of styrene comonomer incorporation: (■) entry 1 (0.0 mol), (●) entry 9 (1.0 mol), (+) entry 10 (1.7 mol) (▲) entry 11 (2.4 mol), (▼) entry 4 (2.9 mol), (×) entry 12 (3.5 mol), and (◆) entry 5 (4.1 mol). The inlet to the figure shows a linear correlation between the crystallization temperature (peak of the distribution) and the styrene content in the copolymers.

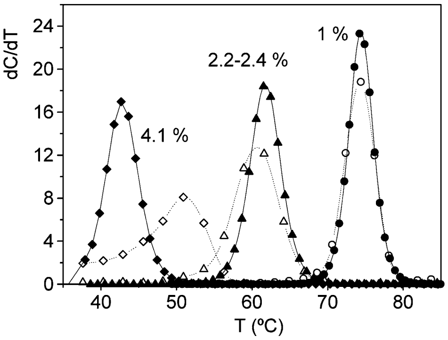


Figure 2. CRYSTAF profiles of poly(ethylene-*co*-styrene) samples obtained from the CGC (open symbols) and norbornane–indenyl (close symbols) catalyst systems exhibiting a range of styrene comonomer incorporation.

meso-**1** are shown in Figure 1. The distribution profiles are all unimodal and extremely narrow. The narrow and symmetrical CRYSTAF profiles illustrated in this figure indicate that no drift takes place during the polymerization reactions irrespective of styrene composition with the norbornane–indenyl catalyst system. This feature of the polymerization reaction points to an interesting homogeneity in the chemical composition of the copolymers obtained. In addition, the correlation between the crystallization temperature and the chemical composition is clear. As it can be observed in the inlet to Figure 1, the crystallization temperature, defined at the peak of the distribution, T_p, decreases linearly as the amount of styrene in the copolymer increases.

On the other hand, the shape of the CCD of copolymers is also different from that obtained in the materials synthesized with CGC. In Figure 2, three pairs of copolymers obtained from both catalyst systems are compared. As it is clearly observed, the copolymers synthesized from norbornane–indenyl catalyst *meso*-**1** show a very homogeneous distribution, which is preserved even for the high styrene content. In the case of CGC system, the CCD broadens as the comonomer content increases.

Conclusion

In this work we describe the synthesis of a new *ansa*-titanocene catalyst derived from norbornane. The inclusion of the bicycle in the structure of the metallocene hinders the movement of the indenyl ligands and, as a result, a highly stereorigid catalyst is obtained and the geometry of the reactive center remains fixed all along the catalytic process. We have tested the activity of this catalyst in ethylene–styrene copolymerization reactions and compared the results with those obtained with CGC (Dow) catalyst. Although incorporation of styrene in the polymer is slightly higher with CGC, we have found that *meso*-**1** is, e.g., 1 order of magnitude more active that CGC and also much more active than other *ansa*-titanocenes and *ansa*-zirconocenes studied by us previously. Further work in order to explore the relation between activity and stereorigidity in norbornane–indenyl metallocenes is actually under way. With this catalyst system is also possible to obtain very high molecular weight polyolefins, as UHMWPE, with very interesting industrial and medical applications. In addition, the CRYSTAF profiles of all the ethylene-*co*-styrene samples obtained from the norbornane–indenyl catalysts are narrower and more symmetric than those obtained with other catalyst system, which is related to unprecedented homogeneous chemical composition of the materials.

Experimental Section

All experiments were carried out under argon atmosphere using flame-dried glassware and standard Schlenk techniques. Anhydrous solvents were distilled under argon from sodium/benzophenone ketyl. ^{1}H and ^{13}C NMR spectra were recorded at 22 °C on Bruker Avance 200-AC (200.1 and 50 MHz) spectrometer. ^{13}C NMR spectra of the polymers were recorded at 100 °C on a Bruker DRX 500 spectrometer operating at 500 MHz. The samples were dissolved in hot 1,2,4-trichlorobenzene (TCB) and benzene-d_6. Carbon signals and styrene contents were assigned according to the literature reference.[10] Chemical shifts are given in ppm relative to TMS (^{1}H, 0.0 ppm) and CDCl$_3$ (^{13}C, 77.0 ppm). Coupling constants are given in hertz. IR spectra were taken on a Perkin-Elmer 781 spectrometer. Average molecular weights M_w and M_n and molecular weight distributions were determined by gel permeation chromatography (GPC) using refractive index RI and viscosity detectors in a Waters 150 CV Gel Permeation Chromatograph. The solvent used for the analysis was TCB, the flow rate was 1.0 mL/min and the temperature was 145 °C. The SEC–viscosity system was calibrated using monodisperse polystyrene standards.

Indene was distilled under argon before use. All other commercially available compounds were used without further purification. 7-Norbornanone was prepared according to literature procedure.[19] 7,7-bis(indenyl)norbornane was prepared from 7-norbornanone following a general procedure described in the literature.[20]

Data for 7,7-Bis(indenyl)norbornane (2): IR (KBr) 3099, 3065, 3043, 2959, 1456, 1392, 1286, 968, 768, 715 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.71 (d, $J = 7.5$ Hz, 2H), 7.39 (d, $J = 7.3$ Hz, 2H), 7.20 (t, $J = 7.3$ Hz, 2H), 7.10 (t, $J = 7.3$ Hz, 2H), 6.66 (t, $J = 2.1$ Hz, 2H), 3.36–3.21 (m, 6H), 2.28–1.73 (m, 4H), 1.40–1.10 (m, 4H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 144.7, 144.4, 143.5, 131.2, 125.3, 123.8, 123.4, 121.6, 57.6, 41.5, 37.4, 28.5; MS (EI) *m/z* 324 (M$^+$, 45), 209 (60), 141 (82), 132 (41), 115 (100), 91 (30), 81 (54).

***rac*- and *meso*-[Norbornane-7,7-bis(indenyl)]titanium Dichloride (*rac*- and *meso*-1).** *n*-Butyllithium (1.6 M in hexane, 4.27 mL, 6.83 mmol) was added by syringe over 10 min to a solution of 1.006 g (3.11 mmol) of **2** in 25 mL of THF at 0 °C. After 30 h at 25 °C the resulting solution was cannulated over a suspension of 479 mg (3.11 mmol) of TiCl$_3$ in 25 mL of THF at 0 °C and the mixture was stirred 24 h at 25 °C. The solvent was evaporated in vacuo and the residue was taken up in 25 mL of CHCl$_3$. Then 50 mL of 6 N HCl were added at −78 °C and the mixture was stirred at 25 °C during 30 min while air was bubbled through. The organic layer was separated and the aqueous solution extracted with CHCl$_3$ (2 × 20 mL). The combined organic solutions were dried over MgSO$_4$ and the solvent was removed under vacuum. The residue was washed with hexane (variable amount of soluble unreacted **2** is recovered) yielding 0.54 g (40%) of **1** (*rac:meso* = 26:74).

meso-**1** is separated and purified from the mixture of isomers by recrystallization from toluene. *meso*-**1**: IR (KBr) 3070, 2959, 1450, 843, 741 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.58 (d, $J = 8.8$ Hz, 2H), 7.49 (d, $J = 8.8$ Hz, 2H), 7.22 (t, $J = 8.5$ Hz, 2H), 7.01 (d, $J = 3.4$ Hz, 2H), 6.88 (t, $J = 7.8$ Hz, 2H), 5.65 (d, $J = 3.4$ Hz, 2H), 3.98 (m, 1H), 3.07 (m, 1H), 2.35−2.10 (m, 4H), 1.95−1.55 (m, 4H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 134.7, 128.3, 127.4, 126.6, 124.8, 124.7, 124.1, 117.6, 93.9, 59.3, 44.8, 40.0, 28.6, 26.4; MS (*m*/*z* (relative intensity); EI, 70 eV) 444 (M$^+$ + 4, 15%), 443 (M$^+$ + 3, 21), 442 (M$^+$ + 2, 64), 441 (M$^+$ + 1, 45), 440 (M$^+$, 86), 405 (M$^+$ − Cl, 44), 404 (M$^+$ − HCl, 100), 322 (M$^+$ − TiCl$_2$, 45), 209 (77), 141 (71); *rac*-**1**: IR (KBr) 3072, 2955, 1452, 843, 814, 745 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.53 (d, $J = 8.7$ Hz, 2H), 7.47−7.41 (m, 4H), 7.04 (dd, $J = 8.8$, 6.6 Hz, 2H), 6.98 (d, $J = 3.4$ Hz, 2H), 5.58 (d, $J = 3.4$ Hz, 2H), 3.44 (m, 2H), 2.31−2.13 (m, 4H), 1.83−1.67 (m, 4H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 134.7, 129.0, 127.9, 126.7, 123.7, 121.3, 120.6, 115.1, 92.8, 59.0, 42.7, 28.7, 26.5; MS (*m*/*z*(relative intensity); EI, 70 eV) 444 (M$^+$ + 4, 14%), 443 (M$^+$ + 3, 20), 442 (M$^+$ + 2, 61), 441 (M$^+$ + 1, 38), 440 (M$^+$, 85), 405 (M$^+$ − Cl, 55), 404 (M$^+$ − HCl, 100), 322 (M$^+$ − TiCl$_2$, 27), 209 (17), 141 (16).

Polymerization Procedures. Copolymerizations were carried out in a 1 L glass autoclave (Büchi AG, Switzerland) prepared before each reaction by heating under vacuum, and then filling with nitrogen to remove impurities. The reactor was then filled with toluene, styrene and half of the required amount of MAO. After thermostating the reactor at the polymerization temperature, nitrogen was removed and the reaction mixture was saturated with ethylene. The rest of the MAO was then added and the reactor was pressurized with ethylene at the polymerization reaction stage. Finally, the catalyst in toluene was injected into the reactor. During polymerization, the ethylene pressure was kept constant and ethylene consumption was measured by a mass flow controller (Brooks Instrument B.V., The Netherlands). The copolymerization was stopped by degassing the reactor to the atmosphere and adding a solution of 20 mL of acidic methanol (containing 5% HCl). Finally, the reaction products were washed with plenty of acidic methanol and acetone, filtered, and dried at 60 °C under vacuum to a constant weight.

CRYSTAF Experiments. During the CRYSTAF experiment, the dissolved polymer is sampled at time intervals and the amount of polymer in the solution is measured, while the temperature of the solution is decreased at a constant cooling rate. For poly(ethylene-*co*-styrene), a copolymer with a lower styrene content will crystallize and precipitate from the solution at a higher temperature than a copolymer with a higher styrene content. A profile obtained from CRYSTAF will reveal not only the level of comonomer incorporation in the polymer, but also the way in which the comonomer is distributed. Chemical composition distributions of the copolymers were determined with a CRYSTAF/TREF instrument model 200+ (PolymerChAR, Spain) equipped with five separate crystallization vessels for simultaneously analyze five different polymeric samples. Samples of 21 mg were dissolved in 30 mL of TCB at a temperature of 160 °C for a total time of 135 min. Then the solutions were allowed to reach thermal equilibrium at 95 °C for another 45 min. Afterward, the solutions were cooled at cooling rate of 0.2 °C/min to 35 °C. The different solutions were sampled 30 times at temperature intervals between 95 and 35 °C, and the concentration of the remaining copolymer in the solutions was measured with a dual-wavelength infrared detector. From the cumulative curves, the CCD distributions shown in Figure 1 are obtained as the simple first derivative function.

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