# Oligomerization of styrenes mediated by cationic allyl nickel complexes containing triphenylstibine or triphenylarsine<sup>†</sup>

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The cationic complexes  $[Ni(\eta^3-CH_2C(R)CH_2)(SbPh_3)_3][BAr'_4]$  (R = CH<sub>3</sub> 1a, H 1b; Ar' = 3,5-C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>),  $[Ni(\eta^3-CH_2C(R)CH_2)(AsPh_3)_2][BAr'_4]$  (R = CH<sub>3</sub> 2a, H 2b),  $[Ni(\eta^3-CH_2CHCH_2)(PPh_3)(L)][BAr'_4]$  (L = SbPh<sub>3</sub> 3, AsPh<sub>3</sub> 4), and the neutral derivatives  $[Ni(\eta^3-CH_2C(R)CH_2)Br(L)]$  (L = SbPh<sub>3</sub>, R = CH<sub>3</sub> 5a, H 5b; L = AsPh<sub>3</sub>, R = CH<sub>3</sub> 6a, H 6b) have been prepared and characterized. The X-ray crystal structures of 1a-b, 2b, 3, 5a and 6b have been determined. These complexes are very active catalyst precursors for the low-molecular weight oligomerization of RC<sub>6</sub>H<sub>4</sub>CH=CH<sub>2</sub> to mainly dimers and trimers of styrene (R = H) or 4-methylstyrene (R = CH<sub>3</sub>). They also catalyse the oligomerization of  $\alpha$ -methylstyrene to dimers and trimers, or to higher oligomers depending upon the reaction conditions (solvent and temperature). The oligomerization reactions were carried out at 25 °C in most cases, in dichloromethane, 1,2-dichloroethane or fluorobenzene, using a olefin/catalyst ratio equal to 2000. The oligomerization products were characterised by means of GPC/SEC.

# Introduction

The use of catalytic systems for olefin polymerization based in nickel complexes bearing N-, O-, or P-donor ligands is well established and it is of wide applicability nowadays.<sup>1-5</sup> Our research group has been working in the synthesis and characterization of allyl nickel complexes bearing bulky phosphine ligands, and in their applications as catalyst precursors for styrene oligomerization and polymerization reactions.<sup>6,7</sup> The catalyst precursors are in general pseudo-square-planar cationic complexes of the type  $[Ni(\eta^3-CH_2C(R)CH_2)(P)_2]^+$  (R = H, Me; (P)\_2 = two monodentate phosphine ligands or one bidentate phosphine ligand).<sup>6,8</sup> Within this context, we have observed that replacement of P donor ligands by either Sb or As donor ligands such as SbPh<sub>3</sub> or AsPh<sub>3</sub> in cationic methylallyl complexes of nickel or leads to systems with display a very high catalytic activity, with turnover frequencies  $N_{\rm t}$  reaching 2052 min<sup>-1</sup>.<sup>9</sup> The products resulting from these nickelcatalysed styrene oligomerization reactions consists of mixtures of low molecular weight oligomers, containing a very high proportion of the head-to-tail dimer of styrene which may represent as much as 88% of the total amount.

The use of SbPh<sub>3</sub> as an alternative to PPh<sub>3</sub> was found to be essential in the modification of the catalyst precursor complex. Thus, the novel tris(stibine) complex [Ni( $\eta^3$ -



 $CH_2C(CH_3)CH_2)(SbPh_3)_3][BAr'_4]$  (Ar' = 3,5-C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>) was isolated and structurally characterised. The smaller cone angle of SbPh<sub>3</sub> compared to AsPh<sub>3</sub> or PPh<sub>3</sub> might favour the adoption of higher coordination numbers in stibine complexes, but its driving force is probably reduced electron donation to the metal centre, which is compensated by binding more ligands.<sup>10</sup> Interestingly, the cationic organonickel–stibine complexes [Ni( $\eta^{5}$ - $C_5H_5$ )(SbR<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>] had been reported years ago, but we found no reports of their applications in catalysis.<sup>11</sup> Very recently, the airstable complexes *trans*-[Ni( $C_6Cl_2F_3$ )<sub>2</sub> $L_2$ ] (L = SbPh<sub>3</sub>, AsPh<sub>3</sub>) have been synthesized. Their catalytic activity in insertion polymerization of norbornene was tested, showing a strong dependence of the yield and molecular mass of the polymer on the ligand used and the solvent.<sup>12</sup> Thus, the highest yield and molecular mass values were obtained using complexes containing SbPh<sub>3</sub> as ligand and non-coordinating solvents. This was attributed to the relative ease of ligand displacement from Ni<sup>II</sup>. In this work we describe the preparation and structural characterization of a series of cationic and neutral allyl and 2-methylallyl nickel complexes bearing SbPh<sub>3</sub> or AsPh<sub>3</sub>, as well as mixed SbPh<sub>3</sub>/PPh<sub>3</sub> and AsPh<sub>3</sub>/PPh<sub>3</sub> ligands. These compounds have shown to be very active as catalyst precursors for the low molecular weight oligomerization of styrene, 4-methylstyrene or  $\alpha$ -methylstyrene without the need of a co-catalyst such as poly(methylalumoxane) (PMAO). The catalytic reactions lead to mixtures of oligomers containing carbon atom chains with lengths ranging from

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 $C_4-C_8$  to  $C_{24}-C_{40}$  depending upon the substrate, the catalyst and the reaction conditions. A preliminary account of this research has already been published.<sup>9</sup>

### **Results and discussion**

#### Preparation of the complexes

The formally five-coordinate cationic complexes  $[Ni(\eta^3-CH_2C(R)CH_2)(SbPh_3)_3][BAr'_4]$  (R = Me 1a, H 1b) were prepared by reaction of  $[{Ni(\eta^3-CH_2C(R)CH_2)(\mu-Br)}_2]$  with SbPh<sub>3</sub> and NaBAr'<sub>4</sub> in fluorobenzene–diethylether, followed by recrystallisation from fluorobenzene–petroleum ether. The analogous reactions using AsPh<sub>3</sub> instead of SbPh<sub>3</sub> led to the formally four-coordinate derivatives  $[Ni(\eta^3-CH_2C(R)CH_2)(AsPh_3)_2][BAr'_4]$ (R = Me 2a, H 2b). Complexes 1a and 2a had been previously obtained by reaction of  $[Ni(\eta^3-CH_2C(CH_3)CH_2)(COD)][BAr'_4]$ with either SbPh<sub>3</sub> or AsPh<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>.



These complexes were isolated in the form of red-purple (1a, 1b) or yellow (2a, 2b) crystalline solids, air-sensitive in solution. A complex formulated as  $[Ni(\eta^3-CH_2CHCH_2)(AsPh_3)_2][PF_6]$  has been briefly mentioned in the literature.<sup>13</sup> In the same report, the yellow-orange material obtained by reaction of  $[Ni(\eta^3 CH_2CHCH_2)_2$  with SbPh<sub>3</sub> and HPF<sub>6</sub> was claimed to be [Ni( $\eta^3$ - $CH_2CHCH_2$ )(SbPh<sub>3</sub>)<sub>2</sub>][PF<sub>6</sub>]. These species were characterised by means of elemental analysis only, and their catalytic activity towards the polymerization of butadiene was studied.<sup>13,14</sup> However, we have never observed in our synthetic work the formation of yellow-orange four-coordinate species of the type [Ni( $\eta^3$ -CH<sub>2</sub>CHCH<sub>2</sub>)(SbPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. Red-purple five-coordinate 1a or 1b was always obtained, irrespective of the number of equivalents of SbPh<sub>3</sub> used in the preparation. Complexes **1a-b** and **2a-b** are diamagnetic, and exhibit in their <sup>1</sup>H NMR spectra well-separated resonances corresponding to the anti and syn protons of the 2-methylallyl or allyl ligands. No coalescence is observed for the resonances of the anti and syn protons when the temperature is raised to 50 °C in CDCl<sub>3</sub> for any of these derivatives, suggesting a relatively high energy barrier for the Hsyn/Hanti exchange process in all these compounds. This contrast with the dynamic behaviour observed for the recently reported five-coordinate allyl derivatives of nickel  $[Ni(\eta^3-CH_2CHCH_2)(P)_3]^+$  (P = PMe<sub>3</sub>, P(OMe)<sub>3</sub>), interpreted in terms of partial PMe<sub>3</sub> or P(OMe)<sub>3</sub> dissociation at ambient temperature, whereas  $\pi$ - $\sigma$  allyl isomerization was found to be insignificant.<sup>15</sup> It appears that a characteristic spectral feature of  $[Ni(\eta^3-CH_2CHCH_2)(P)_3]^+$  complexes is that the  ${}^{13}C{}^{1}H$  NMR chemical shift for the central carbon atom of the allyl ligand (C(2)) is shifted to higher field ( $\delta(C) \approx 90$  ppm) compared to the value in four-coordinate  $[Ni(\eta^3-CH_2CHCH_2)(P)_2]^+$  derivatives  $(\delta(C) > 105 \text{ ppm})$ .<sup>15</sup> In the case of complexes **1a–b**, the value of  $\delta$  for the C(2) atoms is respectively 126.8 and 117.9 ppm. These values are greater than the reported shifts for the resonance of C(2) in  $[Ni(\eta^3-CH_2CHCH_2)(P)_3]^+$ . Furthermore, the chemical shift values for the resonance of C(2) in the four-coordinate complexes

**2a–b** are very similar to those for **1a–b**: 125.9 and 116.2 ppm. There seem to be slight differences in  $\Delta\delta$  (difference between the chemical shifts of the <sup>13</sup>C{<sup>1</sup>H} NMR resonance of C(2) and the resonance of the other two allyl carbon atoms C(1)/C(3)) for five–coordinate stibine complexes ( $\Delta\delta(1a)$  65.2 ppm;  $\Delta\delta(1b)$ 57.8 ppm) and for four-coordinate arsine complexes ( $\Delta\delta(2a)$ 55.8 ppm;  $\Delta\delta(2b)$  45.2 ppm). In any case, these values are never as small as 33–35 ppm, which is the value considered characteristic for [Ni( $\eta^3$ -CH<sub>2</sub>CHCH<sub>2</sub>)(P)<sub>3</sub>]<sup>+</sup> complexes.<sup>15</sup> This means that this spectral feature seems to be restricted to five-coordinate allyl nickel complexes bearing phosphorus-donor ligands.

The X-ray crystal structures of **1b** and **2b** have been determined. The structure of **1a** is also known and was already reported by us.<sup>9</sup> ORTEP views of the cation complexes [Ni( $\eta^3$ -CH<sub>2</sub>CHCH<sub>2</sub>)(SbPh<sub>3</sub>)<sub>3</sub>]<sup>+</sup> and [Ni( $\eta^3$ -CH<sub>2</sub>CHCH<sub>2</sub>)(AsPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> are respectively shown in Fig. 1 and 2, together with the most relevant bond distances and angles.



**Fig. 1** ORTEP drawing (50% thermal ellipsoids) of the complex cation  $[Ni(\eta^3-CH_2CHCH_2)(SbPh_3)_3]^*$  in **1b**. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses: Ni–C(2) 2.007(2), Ni–C(3) 2.115(2), Ni–C(1) 2.089(2), Ni–Sb(1) 2.5059(3), Ni–Sb(2) 2.4627(7), Ni–Sb(3) 2.5684(7), C(1)–C(2) 1.407(3), C(2)–C(3) 1.403(3), Sb(1)–Ni–Sb(2) 102.22(1), Sb(1)–Ni–Sb(3) 106.38(1), Sb(2)–Ni–Sb(3) 105.33(1), C(1)–C(2)–C(3) 117.5(2).

The crystal structure of 1b consists of separate anion and cation moieties, and it contains one dichloromethane solvate molecule. The complex cation in 1b has a pseudo-tetrahedral structure considering the three Sb atoms and the central carbon atom of the allyl unit C(2). It results very similar to the structure adopted by the methylallyl derivative 1a, already reported by us.<sup>9</sup> For 1a we remarked the unsymmetrically-bonded 2-methylallyl (Ni–C(1) 2.228(9) Å, Ni–C(3) 2.076(5) Å). However, for **1b** the allyl ligand appears much more symmetrically arranged (Ni-C(1) 2.089(2) Å, Ni–C(3) 2.115(2) Å), with a shorter Ni–C(2) separation of 2.007(2) Å. These differences could be simply attributed to the fact that the X-ray data collection for 1a was measured at 297 K, whereas for 1b the data collection was carried out at 100 K. All the Sb–Ni–Sb bond angles lie in the narrow interval 102° to 107°. The Ni-Sb separations are similar to those found in 1a, being slightly shorter than the value of 2.4480(6) Å reported for Ni-Sb in  $[Ni(C_6Cl_2F_3)_2(SbPh_3)_2]$ , the only other Ni–SbPh<sub>3</sub> complex structurally characterised to date.<sup>12</sup> Recently, the solid-state structures



Fig. 2 ORTEP drawing (50% thermal ellipsoids) of the complex cation  $[Ni(\eta^3-CH_2CHCH_2)(AsPh_3)_2]^*$  in **2b**. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses: Ni–C(2a) 1.965(6), Ni–C(3) 2.029(5), Ni–C(1) 2.022(4), Ni–As(1) 2.2955(9), Ni–As(2) 2.3150(10), C(1)–C(2a) 1.386(8), C(2a)–C(3) 1.307(8), As(1)–Ni–As(2) 102.62(3), C(1)–C(2a)–C(3) 125.6(7).

of a series of five-coordinate allyl derivatives of nickel [Ni( $\eta^3$ - $CH_2CHCH_2)(triphos)$  [BPh<sub>4</sub>] (triphos = PPh(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>),<sup>16</sup> and  $[Ni(\eta^3-CH_2CHCH_2)(P)_3][X]$  (P = PMe<sub>3</sub>, P(OMe)<sub>3</sub>; X =  $CF_3SO_3^-$ ,  $PF_6^-$ ,  $Br^-$ ,  $I^-$ )<sup>15</sup> have been reported and studied in detail. These structures were interpreted in terms of distorted trigonalbipyramidal (TBP) or square-pyramidal (SPY) geometries as a function of the angular parameter  $\tau$ .<sup>17</sup> For **1b** the value of  $\tau$  is 0.39, consistent with a heavily distorted TBP geometry for the complex cation. In contrast with this, the parameter  $\tau$  has a value of 0.09 for 1a, which indicates that the structure can be better interpreted in terms of a distorted square pyramid, with Sb(3) in the apical position. The structure of the complex cation 2b is pseudo-square planar, very similar to those of the structurally-related cationic phosphine complexes [Ni(n<sup>3</sup>-CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>)(P<sup>i</sup>Pr<sub>2</sub>Ph)<sub>2</sub>][BPh<sub>4</sub>]<sup>6</sup> or [Ni(ŋ<sup>3</sup>-CH<sub>2</sub>CHCH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>],<sup>18</sup> but bearing AsPh<sub>3</sub> instead of tertiary phosphines. The Ni-C and Ni-As separations suggest a fairly symmetrical arrangement of the arsines and the allyl ligand. However, the bond distance C(1)-C(2a) is significantly longer than the corresponding to C(2a)-C(3). The Ni-As bond distances are very similar to the value observed for the complex  $[Ni(C_6Cl_2F_3)_2(AsPh_3)_2]$  (2.3094(7) Å),<sup>12</sup> but slightly longer that the value found for the Ni-As bond distance of 2.2552(10) Å in the cluster compound [(η<sup>5</sup>-MeC<sub>5</sub>H<sub>4</sub>)<sub>3</sub>Mo<sub>3</sub>S<sub>4</sub>Ni(AsPh<sub>3</sub>)][p-TolylSO<sub>3</sub>].<sup>19</sup> The angle formed by the least squares planes defined by the allyl ligand and the plane defined by the NiAs<sub>2</sub> moiety is of 59.8°.

We were interested in preparing complexes containing mixed phosphine–arsine, phosphine–stibine, or arsine–stibine ligands. Thus, we carried out the reactions of complexes **1a** and **1b** with one equivalent of AsPh<sub>3</sub>, in an attempt to prepare the mixed arsine–stibine derivatives. However, the only isolable compounds from these reaction mixtures were the corresponding bis(triphenylarsine) derivatives **2a** or **2b**. No reaction was observed between these compounds and SbPh<sub>3</sub>, even when an excess amount of stibine was used. It is clear that AsPh<sub>3</sub> is far better ligand than SbPh<sub>3</sub> in nickel complexes. For the preparation of

mixed phosphine-stibine and phosphine-arsine complexes, we used a different approach. We carried out the reactions of  $[Ni(\eta^3 CH_2CHCH_2)Br(PPh_3)$  with one equivalent of SbPh<sub>3</sub> or AsPh<sub>3</sub> and NaBAr'<sub>4</sub> in fluorobenzene. From these reactions, crystalline vellow-orange materials were obtained. Their elemental analyses were not entirely satisfactory considering a formulation as  $[Ni(\eta^3 CH_2CHCH_2)(PPh_3)(L)[BAr'_4] (L = SbPh_3, AsPh_3). The {}^{31}P{}^{1}H{}$ NMR spectra of these materials showed two singlet resonances of similar intensity, suggesting the presence of two different phosphorus-containing species. The <sup>1</sup>H NMR spectra showed in each case two sets of allyl proton resonances, in the intensity ratios 3:1 for the SbPh<sub>3</sub> derivative, and 1:1 for the AsPh<sub>3</sub> derivative. Upon recrystallisation, a change in the relative intensity of the <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR signal sets was observed. A X-ray crystal structure analysis of the stibine derivative revealed that these species can be viewed as compounds of composition  $[Ni(\eta^{3}-CH_{2}CHCH_{2})(PPh_{3})_{x}(L)_{1-x}][BAr'_{4}]$  (L = SbPh<sub>3</sub> 3, AsPh<sub>3</sub> 4) where x = 0.75. In these species, a number of PPh<sub>3</sub> ligands has been replaced by either SbPh3 or AsPh3 molecules with little structural distortion, making feasible the crystalization. This can be rationalised considering that these compounds are salts containing one  $[Ni(\eta^3-CH_2CHCH_2)(PPh_3)(L)]^+$  (L = SbPh<sub>3</sub>, AsPh<sub>3</sub>) cation, one  $[Ni(\eta^3-CH_2CHCH_2)(PPh_3)_2]^+$  cation, and two  $[BAr'_4]^-$  anions. Hence, **3** and **4** might be also formulated as  $[Ni(\eta^3 CH_2CHCH_2)(PPh_3)(L)$ [[Ni( $\eta^3$ -CH<sub>2</sub>CHCH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>][BAr'<sub>4</sub>]<sub>2</sub> (L = SbPh<sub>3</sub> 3, AsPh<sub>3</sub> 4). Fig. 3 shows an ORTEP view of the cation complex  $[Ni(\eta^3-CH_2CHCH_2)(PPh_3)(SbPh_3)]^+$  in compound 3, together with the most relevant bond distances and angles for this species.



Fig. 3 ORTEP drawing (50% thermal ellipsoids) of the complex cation  $[Ni(\eta^3-CH_2CHCH_2)(PPh_3)(SbPh_3)]^+$  in 3. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses: Ni–C(2a) 1.962(12), Ni–C(3) 2.045(7), Ni–C(1) 2.010(8), Ni–Sb(1) 2.370(6), Ni–P(1) 2.1915(19), C(1)–C(2a) 1.400(16), C(2a)–C(3) 1.295(14), Sb(1)–Ni–P(1) 102.9(3), C(1)–C(2a)–C(3) 124.5(14).

The structure of the cation  $[Ni(\eta^3-CH_2CHCH_2)(PPh_3)(SbPh_3)]^+$ is pseudo-square planar, and almost identical to that of the cation  $[Ni(\eta^3-CH_2CHCH_2)(PPh_3)_2]^+$  also present in the same crystal. The SbPh<sub>3</sub> and PPh<sub>3</sub> are disordered, and their respective occupation factors were refined to the values of 0.46 for Sb, and 0.54 for P. The Ni–P and Ni–Sb bond distances were constrained. The allyl ligand shows two possible orientations, with two alternative positions for the central carbon atom C(2). It is interesting to point out the fact that if SbPh<sub>3</sub> replaces PPh<sub>3</sub> to give these crystals, then the steric differences between the two ligands might be not so great. In summation, the systems **3** and **4** contain the bis(phosphine) allyl complex  $[Ni(\eta^3-CH_2CHCH_2)(PPh_3)_2]^+$  plus the corresponding cation  $[Ni(\eta^3-CH_2CHCH_2)(L)(PPh_3)]^+$  (L = SbPh<sub>3</sub> or AsPh<sub>3</sub>). In the case of **3**, the two cations crystallize in the same cell in the ratio 1:1. Everything points out that the triphenylarsine derivative **4** behaves similarly. In this fashion, the presence of two sets of allyl resonances in the <sup>1</sup>H NMR spectra, and of two signals in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra can be easily rationalised.

We have isolated the neutral complexes  $[Ni(\eta^3 CH_2C(R)CH_2)Br(EPh_3)$ ] (R = Me, E = Sb 5a, As 6a; R = H, E = Sb 5b, As 6b) by reaction of  $[{Ni(\eta^3-CH_2C(R)CH_2)(\mu-$ Br)<sub>2</sub>] (R = Me, H) with either SbPh<sub>3</sub> or AsPh<sub>3</sub> in diethylether. These compounds were obtained in form of dark red crystalline materials. These species are very air-sensitive in solution, where they are readily decomposed. This makes difficult the recording of good quality NMR spectra due to the formation of paramagnetic impurities. Therefore, great care has to be taken in the manipulation of these compounds with rigurous oxygen exclusion. The X-ray crystal structures of 5a and 6a have been determined. ORTEP views of the complexes  $[Ni(\eta^3-CH_2C(CH_3)CH_2)-$ Br(SbPh<sub>3</sub>)] and [Ni( $\eta^3$ -CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>)Br(AsPh<sub>3</sub>)] are respectively shown in Fig. 4 and 5, together with the most relevant bond distances and angles.



Fig. 4 ORTEP drawing (50% thermal ellipsoids) of the complex  $[Ni(\eta^3-CH_2(CH_3)CH_2)Br(SbPh_3)]$  (5a). Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses: Ni–C(2) 1.990(7), Ni–C(1) 2.000(7), Ni–C(3) 2.012(7), Ni–Sb 2.4558(9), Ni–Br 2.3189(12), C(1)–C(2) 1.404(11), C(2)–C(3) 1.390(11), C(2)–C(4) 1.503(12), Sb–Ni–Br 94.91(4), C(1)–C(2)–C(3) 114.7(8).

The crystal structures of complexes **5a** and **6a** consist of discrete molecules. The co-ordination geometry around nickel is pseudo-square-planar as expected for monomeric 16-electron  $\eta^3$ -allyl complexes. The methylallyl ligands appear fairly symmetrically bonded, with average Ni–C separations close to 2 Å in all cases. The Ni–Sb and Ni–As bond distances have values that compare



Fig. 5 ORTEP drawing (50% thermal ellipsoids) of the complex  $[Ni(\eta^3-CH_2(CH_3)CH_2)Br(AsPh_3)]$  (6a). Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses: Ni–C(1) 1.992(3), Ni–C(2) 1.996(3), Ni–C(3) 2.022(3), Ni–As 2.3128(6), Ni–Br 2.3302(6), C(1)–C(2) 1.393(5), C(2)–C(3) 1.390(5), C(2)–C(4) 1.516(6), As–Ni–Br 97.279(18), C(1)–C(2)–C(3) 114.9(3).

well with those obtained respectively for compounds 1a-b and 2b. The angle As–Ni–Br in 6a has a value of 97.279(18)°, whereas the angle Sb–Ni–Br in 5a is 94.92(4)°. These slight but significant differences might be attributed to the lesser steric pressure of the SbPh<sub>3</sub> ligand due to its smaller cone angle when compared to AsPh<sub>3</sub>. Bromide abstraction from complexes 5a-b and 6a-b using NaBAr'<sub>4</sub> in fluorobenzene leads to highly reactive cationic species which were not isolated, but used *in situ* as catalytic precursors for the oligomerization of styrenes.

### **Oligomerization reactions**

The cationic allyl and methylallyl derivatives 1 to 4 are extremely active catalytic precursors for the low-molecular weight oligomerization of styrene, just as we had already reported for compounds 1a and 2a.<sup>9</sup> The neutral derivatives 5a-b or 6a-b plus one equivalent of NaBAr'<sub>4</sub> in fluorobenzene are also very effective catalytic systems for styrene oligomerization. In these systems, highly reactive 14-electron cationic species of the type  $[Ni(\eta^{3}-CH_{2}C(R)CH_{2})Ni(L)]^{+}$  (R = Me, H; L = SbPh<sub>3</sub>, AsPh<sub>3</sub>)<sup>20</sup> are generated in situ. The catalytic reactions are carried out in noncoordinating solvents such as dichloromethane, fluorobenzene or 1,2-dichloroethane. The reactions are in general highly exothermic and may cause the solvent to boil. The yields of recovered oligomer mixtures are high, as shown in Table 1. In this Table we can appreciate that the oligomer mixtures have a very high content of head-to-tail styrene dimers, which may represent up to 79% of the total (entry 1). Dimer contents are much higher when SbPh<sub>3</sub>-containing catalyst are used (entries 1, 2, 7 and 8). In the case of AsPh<sub>3</sub>-containing catalysts, the amounts of styrene dimer are not as high, and there is a clear increase in the amounts of styrene trimer and higher oligomers (entries 3, 4, 9 and 10). The behaviour of the mixed-ligand complexes 3 and 4 is clearly different. In contrast with the other entries in Table 1, the resulting oligomers contain little styrene dimer and trimer, and the main fraction corresponds to oligomers having  $M_n$  values of 700–726 Da (entries 5 and 6). These

		Solvent	X7: 11a	Product	duct distribution <sup>b</sup> (%)			
Entry	Catalyst		(%)	Dimer	Trimer	Oligomers		
1	1a	CH <sub>2</sub> Cl <sub>2</sub>	100	79	17	4		
2	1b	$CH_2Cl_2$	98	64	23	13		
3	2a	$CH_2Cl_2$	100	53	27	17		
4	2b	$CH_2Cl_2$	100	57	19	24		
5	3	$CH_2Cl_2$	100	12	17	71 <sup>c</sup>		
6	4	$CH_2Cl_2$	75	12	15	65 <sup>d</sup>		
7	5a/NaBAr' <sub>4</sub>	C <sub>6</sub> H <sub>5</sub> F	100	70	22	8		
8	5b/NaBAr' <sub>4</sub>	C <sub>6</sub> H <sub>5</sub> F	95	70	25	5		
9	6a/NaBAr' <sub>4</sub>	C <sub>6</sub> H <sub>5</sub> F	84	42	27	24		
10	6b/NaBAr' <sub>4</sub>	$C_6H_5F$	98	47	31	22		

Experimental conditions: temperature 25 °C, solvent (4 mL), [styrene]/[Ni]= 2000.<sup>*a*</sup> After 45 min. <sup>*b*</sup> Determined by GPC/SEC. Estimated by area integration of the distribution peaks in the GPC/SEC chromatogram. <sup>*c*</sup> Corresponds to an oligomer of  $M_w = 830$ ,  $M_n = 700$ ,  $M_w/M_n = 1.19$ . <sup>*d*</sup> Corresponds to an oligomer of  $M_w = 854$ ,  $M_n = 726$ ,  $M_w/M_n = 1.18$ .

values are almost identical to those obtained when the catalytic oligomerization of styrene is carried out using the complex [Ni( $\eta^3$ -CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> as precursor catalyst.<sup>21,22</sup> This result is not surprising, given the fact that compounds 3 and 4 contain  $[Ni(\eta^3-CH_2CHCH_2)(PPh_3)_2]^+$  cations in their structures, along with variable amounts of  $[Ni(\eta^3-CH_2CHCH_2)(PPh_3)(L)]^+$  species  $(L = SbPh_3 \text{ or } AsPh_3)$ . This indicates that the presence of  $SbPh_3$ or AsPh<sub>3</sub> has little effect on the catalytic properties of the PPh<sub>3</sub>containing system, which remain essentially unaltered. We have also studied the catalytic oligomerization of the styrene derivatives 4-methylstyrene and  $\alpha$ -methylstyrene, in order to establish the effect of methyl substituents on the catalytic activity and in the resulting oligomer distribution. The details of these reactions are summarized in Tables 2 and 3. The oligomerization reactions of 4-methylstyrene (Table 2) were carried out in 1,2-dichloroethane in some instances. Although these reactions parallel in general the behaviour observed with styrene in terms of activity, there is a clear increase in the oligomerization degree. 4-Methylstyrene dimers and trimers are always present. The structure of the dimer corresponds the head-to-tail isomer as in the case of styrene, as inferred from NMR spectroscopy.



In addition to these, there is evidence for the presence of higher oligomers having  $M_n$  in the range 611 to 960. In one case (Table 2, entry 3), a small amount of a polymer with  $M_n = 4467$  has been obtained. This suggests that another different reaction pathways might be also operating here, leading to higher molecular weight oligomers or even polymers. The occurrence of two alternative reaction pathways in the styrene oligo- and polymerization reactions mediated by cationic allyl or indenyl nickel phosphine complexes has been already reported in the recent literature.<sup>6,7,18</sup> The formation of higher molecular

 Table 2
 Oligomerization of 4-methylstyrene catalyzed by complexes 1–6

		Solvent	Yield <sup>a</sup> (%)	Oligomer (GPC data) <sup>b</sup>			
Entry	Catalyst			$M_{ m w}$	$M_{\rm n}$	$I_{p}^{c}$	%
1	1a	CH <sub>2</sub> Cl <sub>2</sub>	95	566	509	1.11	41
				255	246	1.04	59
2	1b	$1,2-C_2H_4Cl_2$	90	719	699	1.03	5
-				445	438	1.02	25
				252	242	1.04	70
3	2a	$CH_2Cl_2$	93	6708	4467	1.50	11
				854	778	1.10	29
				444	436	1.02	30
				258	250	1.03	30
4	2b	$1,2-C_2H_4Cl_2$	93	754	716	1.05	30
				438	431	1.02	34
				254	245	1.04	36
5	3	$CH_2Cl_2$	70	1199	960	1.25	83
5				399	393	1.02	11
				247	242	1.02	6
6	4	$CH_2Cl_2$	63	1179	944	1.25	82
0				396	390	1.01	11
				243	238	1.02	7
7	5a/NaBAr' <sub>4</sub>	C <sub>6</sub> H <sub>5</sub> F	98	636	611	1.04	16
				403	398	1.01	26
				237	228	1.04	58
8	5b/NaBAr' <sub>4</sub>	C <sub>6</sub> H <sub>5</sub> F	98	727	690	1.05	14
				435	428	1.02	29
				251	242	1.04	57
9	6a/NaBAr' <sub>4</sub>	C <sub>6</sub> H <sub>5</sub> F	94	721	666	1.08	36
				397	391	1.01	30
				235	229	1.03	34
10	6b/NaBAr' <sub>4</sub>	C <sub>6</sub> H <sub>5</sub> F	97	786	724	1.09	39
				417	409	1.02	36
				244	236	1.04	25

Experimental conditions: temperature 25 °C, solvent (4 mL), [4-methylstyrene]/[Ni]= 2000.<sup>*a*</sup> After 45 min. <sup>*b*</sup>% estimated by area integration of the distribution peaks in the GPC/SEC chromatogram. <sup>*c*</sup> $I_p = M_w/M_n$  (polydispersity index).

weight oligomers results more evident in the oligomerization reactions of  $\alpha$ -methylstyrene (Table 3). At variance with reactions involving styrene and 4-methylstyrene, we have observed that the characteristics of the oligomers of  $\alpha$ -methylstyrene obtained in the catalytic reactions depend upon the reaction conditions, most notably reaction time, temperature and solvent used. Besides, not all the catalyst precursors studied in the present work showed to be active towards  $\alpha$ -methylstyrene. These have not been included in Table 3. Clearly, the presence of a methyl group at the  $\alpha$ -position of the styrene has a deactivating effect towards the catalytic effectiveness of most of the compounds studied. Complexes 1a-b and 2a-b catalyse the very low molecular weight oligomerization (mainly dimerization and trimerization) of  $\alpha$ -methylstyrene when the reactions are performed in 1,2-dichloroethane at 50 °C for a period of 24 h (Table 3, entries 1, 3, 5 and 6). At variance with this, when the reactions were carried out in dichloromethane at 25 °C, higher oligomers were obtained, having  $M_n$  in the range 1398–2373 Da and with polydispersities  $I_p$  in between 1.85 and 3.36. A similar product distribution was obtained in the reactions using neutral catalyst precursors plus NaBAr'<sub>4</sub> in fluorobenzene at 25 °C. Hence, the use of dichloromethane or fluorobenzene at room temperature favours the formation of higher oligomers composed mainly of carbon chains containing 24 to 40 carbon atoms ( $C_{24}$ – $C_{40}$ ). In sharp contrast with this, the use of 1,2-dichoroethane, higher temperatures and longer reaction times lead to the formation of

Table 3	Oligomerization of	f α-methylstyrene	catalyzed by	complexes 1-6
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Entry	Catalyst		T∕°C	Time	Yield (%)	Polymer (GPC data) <sup>a</sup>			
		Solvent				$\overline{M_{ m w}}$	${M}_{ m n}$	$I_{\mathrm{p}}{}^{b}$	%
1	1a	$1,2-C_2H_4Cl_2$	50	24 h	100	357	343	1.04	73
						217	213	1.02	27
2	1b	$CH_2Cl_2$	25	45 min	90	3944	2062	1.91	68
						434	403	1.08	21
						210	207	1.02	6
3	1b	$1,2-C_2H_4Cl_2$	50	24 h	100	524	513	1.02	3
						353	349	1.01	20
						221	212	1.04	73
4	2a	$CH_2Cl_2$	25	45 min	57	4696	1398	3.36	100
5	2a	$1,2-C_2H_4Cl_2$	50	24 h	72	363	345	1.05	77
						214	211	1.02	33
6	2b	$1,2-C_2H_4Cl_2$	50	24 h	100	405	395	1.03	16
						231	221	1.04	83
7	5a/NaBAr' <sub>4</sub>	C <sub>6</sub> H <sub>5</sub> F	25	45 min	58	3400	1934	1.76	69
						471	451	1.04	15
						235	228	1.03	16
8	5b/NaBAr' <sub>4</sub>	$C_6H_5F$	25	45 min	56	4385	2373	1.85	65
						474	441	1.07	19
						221	214	1.03	10
9	6b/NaBAr' <sub>4</sub>	$C_6H_5F$	25	16 h	60	6453	2204	2.93	100

Experimental conditions: solvent (4 mL), [ $\alpha$ -methylstyrene]/[Ni] = 2000. "% estimated by area integration of the distribution peaks in the GPC/SEC chromatogram."  $I_p = M_w/M_n$  (polydispersity index).

dimers and trimers of  $\alpha$ -methylstyrene. It is important to note here that the structure of the dimer of  $\alpha$ -methylstyrene is not homologous to that of the dimers of styrene or 4-methylstyrene obtained with the same catalyst precursors. NMR data suggest that in this case the dimer can be formally viewed as the product of insertion of one  $\alpha$ -methylstyrene into one of the C–H bonds of the methyl substituent at the  $\alpha$ -position:



The insertion mechanism proposed for the oligomerization of styrenes mediated by cationic allyl-phosphine complexes<sup>7,8,21</sup> can be easily adapted to explain the oligomerization reactions using allylnickel complexes bearing SbPh<sub>3</sub> or AsPh<sub>3</sub> ligands. Such mechanism involves addition of styrene to a Ni–H bond to yield a styryl complex (proposed to be bound to the nickel center in an  $\eta^3$ -benzylic fashion<sup>22</sup>) which by multiple insertion and subsequent  $\beta$ -hydride elimination gives rise to head-to-tail polystyrene chains containing methyl and unsaturated end-groups (Scheme 1).

In the case of  $\alpha$ -methylstyrene, the cycle in Scheme 1 has to be modified in order to account for the observed differences in the structure of the resulting products. A reasonable explanation consistent with the experimental observations would be to consider an alternative structure for the  $\eta^3$ -styryl complex. It seems very likely that in the particular case of  $\alpha$ -methylstyrene, the  $\eta^3$ -styryl intermediate would adopt a symmetric structure as shown in Scheme 2, which does not require the direct involvement of the bonds in the aromatic cycle. The formation of such a species, namely [Ni( $\eta^3$ -CH<sub>2</sub>C(C<sub>6</sub>H<sub>3</sub>)CH<sub>2</sub>)(EPh<sub>3</sub>)( $\eta^2$ -CH<sub>2</sub>C(CH<sub>3</sub>)Ph)]<sup>+</sup>, involves the concomitant evolution of hydrogen as an alternative to the insertion step proposed in Scheme 1.

One of the key steps in these catalytic processes is the generation of the highly reactive 14-electron species of the type  $[Ni(\eta^{3}-CH_{2}C(R)CH_{2})(EPh_{3})]^{+}$  (R = Me, H; E = Sb, As). These are generated directly by bromide abstraction from the neutral complexes 5a-b or 6a-b, or by dissociation from the respective cationic tris(stibine) or bis(arsine) complexes. Since the bis(arsine) complexes 2a-b are coordinatively unsaturated 16-electron species, the dissociation of AsPh<sub>3</sub> does not seem in principle imperative for their participation in the catalytic cycle. However, we have noticed that addition of AsPh<sub>3</sub> to the catalytic reaction mixture has a noticeable effect on the activity. The yields of isolated oligomers drop drastically when the amount of added AsPh<sub>3</sub> is increased. With 5 equivalents of AsPh<sub>3</sub> per equivalent of catalyst precursor, the catalytic activity is totally suppressed. Given the fact that the 2a-b do not add a third AsPh<sub>3</sub> molecule to furnish the corresponding tris(arsine), we assume that the addition of AsPh<sub>3</sub> produces a shift in the initial ligand dissociation equilibrium. In this manner, the formation of the 14-electron species is inhibited and the catalytic cycle can not be initiated. The addition of SbPh<sub>3</sub> to 1a-b has a similar effect on their catalytic activity, this being also suppressed upon the addition of 5 equivalents of SbPh<sub>3</sub>.

The observed oligomer distribution can be explained in almost all cases by the reaction sequence involving insertion of the olefin into the Ni–H bond and subsequent chain growth, followed by a  $\beta$ -elimination as shown in Scheme 1. Alternatively, for  $\alpha$ -methylstyrene the insertion would occur into the Ni–C of the symmetric  $\eta^3$ -styryl intermediate (Scheme 2). A fast  $\beta$ -elimination favours low-molecular weight oligomers (dimers and trimers). If the chain growth reactions are faster, then higher molecular weight oligomers should be expected. The balance of the rates of these reactions is dependant on the nature of the substrate, judging from our results, but also on the temperature at which





the reactions are performed. Since higher temperatures favour the formation of dimers and trimers this indicates that the  $\beta$ elimination is faster and hence the controlling step in the process is the chain growth reaction. Opposite to this, lower temperatures favour the formation of higher oligomers, indicative of a increase of the rate of the chain growth reactions relative to the  $\beta$ elimination step. Both the insertion and the chain growth reactions are expected to have negative values of the activation entropy  $\Delta S^{\ddagger}$ , whereas positive values are expected for the  $\beta$ -elimination reaction. Assuming positive values of  $\Delta H^{\ddagger}$ , this means that the variation of the relative reaction rates with the temperature is just as expected. This is fully consistent with the observed dependence of the oligomerization degree with the temperature in our case. The occurrence of another alternative oligomerization mechanism (*i.e.* cationic oligomerization) can not be ruled out in principle, but it does not seem strictly necessary to invoke it in order to explain satisfactorily the observed oligomer distribution in these catalytic reactions.

## Conclusions

Triphenylstibine and triphenylarsine constitute interesting alternatives to the use of more traditional tertiary phosphine ligands in cationic allylnickel complexes with applications in catalytic styrene oligomerization reactions. With SbPh<sub>3</sub>, formally five-coordinate species of the type [Ni( $\eta^3$ -CH<sub>2</sub>C(R)CH<sub>2</sub>)(SbPh<sub>3</sub>)<sub>3</sub>]<sup>+</sup> (R = Me, H) are formed, in contrast with the formally square-planar species [Ni( $\eta^3$ -CH<sub>2</sub>C(R)CH<sub>2</sub>)(L)<sub>2</sub>]<sup>+</sup> (R = Me, H; L = AsPh<sub>3</sub>, PPh<sub>3</sub>). The allylnickel complexes containing SbPh<sub>3</sub> or AsPh<sub>3</sub> as coligands are extremely efficient catalyst precursors for the very low

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Scheme 2

molecular weight oligomerization of styrenes. In general terms, the use of SbPh<sub>3</sub> as co-ligand leads to a decrease in the degree of styrene oligomerization (mostly dimers) in comparison with similar systems with PPh<sub>3</sub>. The degree of styrene oligomerization when AsPh<sub>3</sub>-containing complexes are used as catalytic precursors can be considered intermediate between those obtained with SbPh<sub>3</sub> and PPh<sub>3</sub>-containing complexes. The nature of the resulting oligomerization products is also dependant on the substituents present on the styrene, as well as the reaction conditions. For styrene and 4-methylstyrene, an insertion mechanism analogous to that proposed for analogue phosphine-containing systems has been suggested. The fast  $\beta$ -elimination reaction step favours dimers and trimers over higher oligomers. Apparently, this can be reversed as a function of the reaction temperature. In the case of  $\alpha$ -methylstyrene the reaction pathway is slightly modified. The participation of a symmetric  $\eta^3$ -styryl intermediate is proposed in order to rationalise the structures observed for the oligomerization products of α-methylstyrene.

## Experimental

All synthetic operations were performed under a dry dinitrogen or argon atmosphere following conventional Schlenk techniques. Tetrahydrofuran, diethyl ether and petroleum ether (boiling point range 40-60 °C) were obtained oxygen- and water-free from an Innovative Technology, Inc. solvent purification apparatus. Toluene and fluorobenzene were of anhydrous quality and used as received. All solvents were deoxygenated immediately before use. The complex [Ni(COD)<sub>2</sub>] was obtained according to the literature.<sup>8</sup> Styrene was purified by treatment with CaH<sub>2</sub> followed by trapto-trap distillation. NMR spectra were taken on a Varian Inova 400 MHz or Varian Gemini 300 MHz equipment. Chemical shifts are given in ppm from SiMe<sub>4</sub> (<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}), or 85% H<sub>3</sub>PO<sub>4</sub>  $({}^{31}P{}^{1}H{})$ . Microanalysis was performed on an elemental analyzer model LECO CHNS-932 at the Servicio Central de Ciencia y Tecnología, Universidad de Cádiz. Molecular weight distributions of oligomers were determined at 25 °C by GPC/SEC using Merck-Lacrom equipment fitted with one column Polystyragel PS40

(10 mm;  $7.8 \times 300$  mm). The oligomer samples were eluted with THF at a flow rate of 1 cm<sup>3</sup> min<sup>-1</sup>. The system was calibrated using a Merck polystyrene standard kit.

### Syntheses

 $[Ni(\eta^3-CH_2C(R)CH_2)(SbPh_3)_3][BAr'_4]$  (R = Me 1a, H 1b). To a slurry of [Ni(COD)<sub>2</sub>] (0.22 g. 0.8 mmol) in diethyl ether (15 mL) cooled to -80 °C in a ethanol/liquid N<sub>2</sub> bath, either 3-bromo-2-methypropene (83.2 µL, 0.8 mmol) or allyl bromide (69.9 µL, 0.8 mmol) was added. The mixture was warmed at room temperature and stirred for 45 min. During this time the slurry changed from yellow to red. The solvent was removed in vacuo, and the solids extracted with fluorobenzene. To this red solution SbPh<sub>3</sub> (0.85 g. 2.4 mmol) and NaBAr'<sub>4</sub> (0.7 g. 0.8 mmol) was added. A color change from red to dark purplebrown was observed. The solution was filtered through Celite, concentrated to 5 mL and petroleum ether (15 mL) was added. The dark purplish-red microcrystalline precipitate was filtered off, washed with petroleum ether, and dried in vacuo. Both complexes were recrystallized from fluorobenzene-petroleum ether (1a) or dichloromethane-petroleum ether (1b, containing one dichloromethane solvate molecule). Data for 1a: yield: 1.14 g, 70%. Calcd. for C<sub>90</sub>H<sub>64</sub>BF<sub>24</sub>NiSb<sub>3</sub>: C, 53.1; H, 3.17%. Found: C, 52.9; H, 3.06%. NMR: <sup>1</sup>H (CD<sub>2</sub>Cl<sub>2</sub>, 298 K) δ 2.04 (s, 3 H, CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>); 2.94 (s br, 2 H, CH<sup>anti</sup>C(CH<sub>3</sub>)CH<sup>anti</sup>); 4.31 (m, 2 H, CH<sup>syn</sup>C(CH<sub>3</sub>)CH<sup>syn</sup>); 7.29, 7.34 (m, 45 H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} (CDCl<sub>3</sub>, 298 K)  $\delta$  23.9 (s, CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>); 65.2 (s, CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>); 117.9 (s, CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>); 129.8, 130.3, 134.0, 135.2 (C<sub>6</sub>H<sub>5</sub>). Data for 1b: yield: 1.28 g, 79%. Anal. Calcd for C<sub>90</sub>H<sub>64</sub>BCl<sub>2</sub>F<sub>24</sub>NiSb<sub>3</sub>: C, 51.3; H, 3.06%. Found: C, 51.6; H, 3.10%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 2.92 (d, 2H,  ${}^{3}J_{\rm HH} = 12.8$  Hz, CH<sup>syn</sup>H<sup>anti</sup>CHCH<sup>syn</sup>H<sup>anti</sup>), 4.30 (d, 2H,  ${}^{3}J_{\rm HH} =$ 6.4 Hz,  $CH^{syn}H^{anti}CHCH^{syn}H^{anti}$ ), 5.71 (psq, 1H,  ${}^{3}J_{HH} = 6.4$  Hz,  $CH^{syn}H^{anti}CHCH^{syn}H^{anti}$ , 7.14, 7.26 (m,  $C_6H_5$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 60.1 (s, CH<sub>2</sub>CHCH<sub>2</sub>),117.9 (s, CH<sub>2</sub>CHCH<sub>2</sub>), 130.1, 130.9, 134.1, 135.2 (*C*<sub>6</sub>H<sub>5</sub>).

 $[Ni(\eta^{3}-CH_{2}C(R)CH_{2})(AsPh_{3})_{2}][BAr'_{4}]$  (R = Me 2a, H 2b). To a slurry of [Ni(COD)<sub>2</sub>] (0.22 g. 0.8 mmol) in diethyl ether (15 mL) cooled to -80 °C in a ethanol/liquid N<sub>2</sub> bath, either 3-bromo-2-methypropene (83.2 µL, 0.8 mmol) or allyl bromide (69.9 µL, 0.8 mmol) was added. The mixture was warmed at room temperature and stirred for 45 min. During this time the slurry changed from yellow to red. The solvent was removed in vacuo, and the solids extracted with fluorobenzene. To this red solution AsPh<sub>3</sub> (0.51 g. 1.6 mmol) and NaBAr'<sub>4</sub> (0.7 g. 0.8 mmol) was added. A color change from red to yellowish brown was observed. The solution was filtered through Celite, concentrated to 5 mL and petroleum ether (15 mL) was added. The resulting yelloworange microcrystalline precipitate was filtered off, washed with petroleum ether, and dried in vacuo. Both complexes were recrystallized from fluorobenzene-petroleum ether. Data for 2a: yield: 0.87 g, 68%. Anal. Calcd for C72H49As2BF24Ni: C, 54.4; H, 3.11%. Found: C, 54.1; H, 3.15%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 2.01 (s, 3H, CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>), 2.80 (s, 2H, CH<sup>syn</sup>H<sup>anti</sup>C(CH<sub>3</sub>)CH<sup>syn</sup>H<sup>anti</sup>), 3.69 (s, 2H, CH<sup>syn</sup>H<sup>anti</sup> C(CH<sub>3</sub>)CH<sup>syn</sup>H<sup>anti</sup>), 7.20, 7.28 (m, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  23.13 (s, CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>), 70.07 (s, CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>), 125.9 (s, CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>), 129.64, 131.15, 131.84, 132.66 (C<sub>6</sub>H<sub>5</sub>). Data for **2b**: yield: 1 g, 78%.

Anal. Calcd for  $C_{71}H_{47}As_2BF_{24}Ni$ : C, 54.1; H, 3.01%. Found: C, 54.3; H, 3.04%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  2.92 (d, 2H, <sup>3</sup> $J_{HH}$  = 14.8 Hz, CH<sup>sym</sup>H<sup>anti</sup>CHCH<sup>sym</sup>H<sup>anti</sup>), 4.11 (d, 2H, <sup>3</sup> $J_{HH}$  = 7.6 Hz, CH<sup>sym</sup>H<sup>anti</sup>CHCH<sup>sym</sup>H<sup>anti</sup>), 5.66 (psq, 1H, <sup>3</sup> $J_{HH}$  = 7.2 Hz, CH<sup>sym</sup>H<sup>anti</sup>CHCH<sup>sym</sup>H<sup>anti</sup>), 7.22, 7.31 (m, C<sub>6</sub> $H_5$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  70.97 (s, CH<sub>2</sub>CHCH<sub>2</sub>),116.2 (s, CH<sub>2</sub>CHCH<sub>2</sub>), 129.97, 131.38, 132.55, 133.25 (C<sub>6</sub>H<sub>5</sub>).

 $[Ni(\eta^3-CH_2CHCH_2)(PPh_3)(L)][Ni(\eta^3-CH_2CHCH_2)(PPh_3)_2]$  $[BAr'_4]_2$  (L = SbPh<sub>3</sub> 3, AsPh<sub>3</sub> 4). To a solution of  $[Ni(\eta^3 -$ CH<sub>2</sub>CHCH<sub>2</sub>)Br(PPh<sub>3</sub>)] (0.25 g. 0.57 mmol) in fluorobenzene (15 mL) either SbPh<sub>3</sub> (0.220 g. 0.57 mmol) or AsPh<sub>3</sub> (0.17 g. 0.57 mmol) and NaBAr'<sub>4</sub> (0.51 g. ca. 0.57 mmol) were added. The mixture was stirred for 45 min at room temperature. During this time the solution changed from red to dark red. Then, the solution was concentrated to 5 mL and petroleum ether (15 mL) was added. The resulting yellow-orange microcrystalline precipitate was filtered off, washed with petroleum ether, and dried in vacuo. Both complexes were recrystallized from fluorobenzene-petroleum ether. Data for 3: yield: 0.66 g, 75%. Calcd. for C<sub>144</sub>H<sub>94</sub>B<sub>2</sub>F<sub>48</sub>Ni<sub>2</sub>P<sub>3</sub>Sb: C, 55.97; H, 3.07%. Found: C, 55.8; H, 3.05%. NMR: Selected data for [Ni( $\eta^3$ -CH<sub>2</sub>CHCH<sub>2</sub>)(PPh<sub>3</sub>)(SbPh<sub>3</sub>)]<sup>+</sup> cation: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  2.93 (d, 2H,  ${}^{3}J_{\rm HH} = 14.4$  Hz, CH<sup>syn</sup>H<sup>anti</sup>CHCH<sup>syn</sup>H<sup>anti</sup>), 4.23 (d, 2H,  ${}^{3}J_{HH} = 6.2$  Hz,  $CH^{syn}H^{anti}CHCH^{syn}H^{anti}$ ), 5.56 (m, 1H, CH<sup>syn</sup>H<sup>anti</sup>CHCH<sup>syn</sup>H<sup>anti</sup>), 7.15–7.32 (m,  $C_6H_5$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 27.66. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 70.63 (s, CH<sub>2</sub>CHCH<sub>2</sub>), 115.29 (s, CH<sub>2</sub>CHCH<sub>2</sub>), 130,10, 130.79, 132.19, 135.84 ( $C_6H_5$ ). Selected data for [Ni( $\eta^3$ -CH<sub>2</sub>CHCH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>)]<sup>+</sup> cation:<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  2.78 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 13.8 Hz, CH<sup>syn</sup>H<sup>anti</sup>CHCH<sup>syn</sup>H<sup>anti</sup>), 3.86 (br, 2H, CH<sup>syn</sup>H<sup>anti</sup>CHCH<sup>syn</sup>H<sup>anti</sup>), 5.60 (m, 1H, CH<sup>syn</sup>H<sup>anti</sup>CHCH<sup>syn</sup>H<sup>anti</sup>), 7.22–7.32 (m, C<sub>6</sub>H<sub>5</sub>).  ${}^{31}P{}^{1}H$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  26.36.  ${}^{13}C{}^{1}H$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 74.78 (s, CH<sub>2</sub>CHCH<sub>2</sub>), 116.98 (s, CH<sub>2</sub>CHCH<sub>2</sub>), 129.51, 129.66, 131.79, 133.54, 133.69 (C<sub>6</sub>H<sub>5</sub>). Data for 4: yield: 0.69 g, 80%. Calcd. for C<sub>144</sub>H<sub>94</sub>AsB<sub>2</sub>F<sub>48</sub>Ni<sub>2</sub>P<sub>3</sub>: C, 56.84; H, 3.11%. Found: C, 56.5; H, 3.09%. NMR: Selected data for [Ni(ŋ<sup>3</sup>- $CH_2CHCH_2)(PPh_3)(AsPh_3)]^+$  cation: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  2.91 (d, 2H,  ${}^{3}J_{\rm HH} = 13.8$  Hz, CH<sup>syn</sup>H<sup>anti</sup>CHCH<sup>syn</sup>H<sup>anti</sup>), 4.11 (d, 2H,  ${}^{3}J_{HH} = 7.7$  Hz,  $CH^{syn}H^{anti}CHCH^{syn}H^{anti}$ ), 5.66 (m, 1H,  $CH^{syn}H^{anti}CHCH^{syn}H^{anti})$ , 7.14–7.45 (m, C<sub>6</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 26.87. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 72.65 (s, CH<sub>2</sub>CHCH<sub>2</sub>), 117.19 (s, CH<sub>2</sub>CHCH<sub>2</sub>), 129.87, 131.13, 132.02, 133.30 ( $C_6H_5$ ). Selected data for  $[Ni(\eta^3-CH_2CHCH_2)(PPh_3)_2)]^+$ cation:<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  2.78 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 13.8 Hz, CH<sup>syn</sup>H<sup>anti</sup>CHCH<sup>syn</sup>H<sup>anti</sup>), 3.86 (br, 2H, CH<sup>syn</sup>H<sup>anti</sup>CHCH<sup>syn</sup>H<sup>anti</sup>), 5.60 (m, 1H, CH<sup>syn</sup>H<sup>anti</sup>CHCH<sup>syn</sup>H<sup>anti</sup>), 7.14–7.45 (m, C<sub>6</sub>H<sub>5</sub>).  ${}^{31}P{}^{1}H$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  26.37.  ${}^{13}C{}^{1}H$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 74.76 (s, CH<sub>2</sub>CHCH<sub>2</sub>), 116.79 (s, CH<sub>2</sub>CHCH<sub>2</sub>), 129.51, 129.66, 131.79, 133.54, 133.69 (*C*<sub>6</sub>H<sub>5</sub>).

[Ni( $\eta^3$ -CH<sub>2</sub>C(R)CH<sub>2</sub>)Br(SbPh<sub>3</sub>)] (R = Me 5a, H 5b). To a slurry of [Ni(COD)<sub>2</sub>] (0.22 g. 0.8 mmol) in diethyl ether (15 mL) cooled to -80 °C a ethanol/liquid N<sub>2</sub> bath, either 3-bromo-2-methypropene (83.2 µL, 0.8 mmol) or allybromide (69.9 µL, 0.8 mmol) was added. The mixture was warmed at room temperature and stirred for 45 min. Then the solvent was removed under vacuum. The residue was extracted with fluorobenzene. To this red solution SbPh<sub>3</sub> (0.35 g. 1 mmol) was added. The solution was filtered through Celite, in order to remove Ni<sup>0</sup>,

most often formed during the reaction. Then the solution was concentrated to 5 mL and petroleum ether (15 mL) was added. The red microcrystalline precipitate was filtered off, and washed with petroleum ether, and dried in vacuo. Both complexes were recrystallized from fluorobenzene-petroleum ether. Data for 5a: yield: 0.27 g, 62%. Calcd. for C<sub>22</sub>H<sub>22</sub>BrNiSb: C, 48.3; H, 4.06%. Found: C, 48.2; H, 3.98%. NMR: <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>, 298 K) δ 1.71 (s, 3 H, CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>); 2.79 (s br, 2 H, CH<sup>anti</sup>C(CH<sub>3</sub>)CH<sup>anti</sup>); 4.31 (s br, 2 H, CH<sup>syn</sup>C(CH<sub>3</sub>)CH<sup>syn</sup>); 7.01, 7.45 (m, 15 H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  22.6 (s, CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>); 57.2 (s, CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>); 129.0 (s, CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>); 129.2, 136.7 (C<sub>6</sub>H<sub>5</sub>). Data for **5b**: yield: 0.25 g, 59%. Calcd. for C<sub>21</sub>H<sub>20</sub>BrNiSb: C, 47.4; H, 3.78%. Found: C, 47.1; H, 3.64%. NMR: <sup>1</sup>H (CD<sub>2</sub>Cl<sub>2</sub>, 298 K)  $\delta$  2.36 (s br, 2 H, CH<sup>anti</sup>CHCH<sup>anti</sup>); 3.51 (d, <sup>3</sup>J<sub>HH</sub> = 12 Hz, 2 H, CH<sup>syn</sup>CHCH<sup>syn</sup>); 5.42 (m, 1 H, CH<sub>2</sub>CHCH<sub>2</sub>); 7.40, 7.55 (m, 15 H,  $C_6H_5$ ).<sup>13</sup>C{<sup>1</sup>H} (CDCl<sub>3</sub>, 298 K)  $\delta$  58.4 (s, CH<sub>2</sub>CHCH<sub>2</sub>); 106.7 (s, CH<sub>2</sub>CHCH<sub>2</sub>); 129.4, 129.8, 134.7, 136.4 (C<sub>6</sub>H<sub>5</sub>).

 $[Ni(\eta^3-CH_2C(R)CH_2)Br(AsPh_3)]$  (R = Me 6a, H 6b). These compounds were prepared by a identical procedure to that for 5a-b, using AsPh<sub>3</sub> (0.31 g, 1 mmol) instead of SbPh<sub>3</sub>. Data for 6a: yield: 0.23 g, 58%. Calcd. for C222H22AsBrNi: C, 52.9; H, 4.44%. Found: C, 52.6; H, 4.24%. NMR: <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>, 298 K) δ 1.87 (s, 3 H,  $CH_2C(CH_3)CH_2$ ; 2.32 (s br, 2 H,  $CH^{anti}C(CH_3)CH^{anti}$ ); 3.25 (s br, 2 H, CH<sup>syn</sup>C(CH<sub>3</sub>)CH<sup>syn</sup>); 7.22, 7.78 (m, 15 H,  $C_6H_5$ ). <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  22.7 (s, CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>); 61.8 (s, CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>); 125.9 (s, CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>); 129.4, 130.3, 134.6, 136.4 (C<sub>6</sub>H<sub>5</sub>). Data for **5b**: yield: 0.23 g, 60%. Calcd. for C<sub>21</sub>H<sub>20</sub>AsBrNi: C, 51.9; H, 4.15%. Found: C, 51.6; H, 4.08%. NMR: <sup>1</sup>H (tetrahydrofuran-d<sub>8</sub>, 298 K)  $\delta$  2.40 (d, <sup>3</sup>J<sub>HH</sub> = 11.2 Hz, 2 H, CHantiCHCHanti); 3.39 (s br, 2 H, CHsynCHCHsyn); 5.44 (m, 1 H, CH<sub>2</sub>CHCH<sub>2</sub>); 7.37, 7.58 (m, 15 H,  $C_6H_5$ ).<sup>13</sup>C{<sup>1</sup>H} (tetrahydrofuran-d<sub>8</sub>, 298 K)  $\delta$  61.3 (s, CH<sub>2</sub>CHCH<sub>2</sub>); 108.7 (s, CH<sub>2</sub>CHCH<sub>2</sub>); 129.4, 130.3, 134.6, 136.4 (C<sub>6</sub>H<sub>5</sub>).

#### X-Ray structure determinations

Crystal data and experimental details are given in Table 4. X-Ray diffraction data for compound 1b were collected on a Bruker AXS SMART Platform 3-circle diffractometer with CCD area detector at the Institute of Chemical Technologies and Analytics, Vienna University of Technology and for compounds 2b, 3, 5a and 6a on a Bruker SMART APEX 3-circle diffractometer with CCD area detector at The Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz, using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Hemispheres of the reciprocal space were measured by omega scan frames with  $\delta(\omega) 0.30^{\circ}$ . Correction for absorption and crystal decay (insignificant) were applied by semi-empirical method from equivalents using program SADABS.23 The structures were solved by direct methods, completed by subsequent difference Fourier synthesis and refined on  $F^2$  by full matrix least-squares procedures using the program SHELXTL.<sup>24</sup> All non-hydrogen atoms except some in disordered groups were anisotropically refined. The hydrogen atoms were placed at geometric positions and refined using the riding model. In compound 3 the main disorder was found in the cation, being approximately in 1:1 ratio bis(phosphine) or phosphine and stibine ligands. Complementary P and Sb atoms were refined to model this disorder. To avoid an averaged bond distance Ru-P and Ru-Sb bond lengths were constrained to reasonable chemical

Compound	1b	2b	3	5a	6a
Formula	C <sub>89.86</sub> H <sub>63.71</sub> BCl <sub>1.71</sub> F <sub>24</sub> NiSb <sub>3</sub>	$C_{71}H_{47}As_2BF_{24}Ni$	C <sub>71</sub> H <sub>47</sub> BF <sub>24</sub> NiP <sub>1.54</sub> Sb <sub>0.46</sub>	C22H22BrNiSb	C <sub>22</sub> H <sub>22</sub> AsBrNi
FW	2094.95	1575.45	1529.56	546.77	499.94
T/K	100(2)	100(2)	100(2)	293(2)	293(2)
Crystal size/mm	$0.65 \times 0.55 \times 0.45$	$0.55 \times 0.12 \times 0.11$	$0.47 \times 0.08 \times 0.07$	$0.45 \times 0.40 \times 0.17$	$0.35 \times 0.30 \times 0.27$
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 1 (no. 2)	<i>P</i> 1 (no. 2)	<i>P</i> 1 (no. 2)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
Cell parameters	a = 13.2682(6) Å	a = 13.038(3)  Å	a = 13.093(3) Å	a = 12.160(2) Å	a = 12.021(2)  Å
•	b = 17.6246(7) Å	b = 14.663(3) Å	b = 14.560(3) Å	b = 10.1466(17)  Å	b = 9.9974(18)  Å
	c = 19.2441(8) Å	c = 17.637(4) Å	c = 17.565(4) Å	c = 17.556(4)  Å	c = 17.404(3) Å
	$\alpha = 68.634(1)^{\circ}$	$\alpha = 74.84(3)^{\circ}$	$\alpha = 75.09(3)^{\circ}$		
	$\beta = 84.927(1)^{\circ}$	$\beta = 81.73(3)^{\circ}$	$\beta = 81.42(3)^{\circ}$	$\beta = 97.557(8)^{\circ}$	$\beta = 98.246(3)^{\circ}$
	$\gamma = 87.387(1)^{\circ}$	$\gamma = 88.15(3)^{\circ}$	$\gamma = 88.28(3)^{\circ}$		
Volume/Å <sup>3</sup>	4174.0(3)	3220.4(11)	3199.4(13)	2147.3(7)	2070.0(6)
Ζ	2	2	2	4	4
$ ho_{\rm c}/{ m g~cm^{-3}}$	1.677	1.625	1.588	1.691	1.604
$\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>	1.347	1.434	0.647	3.997	4.455
F(000)	2068	1576	1537.3	1072	1000
Max. and min. transmission factors	0.845-1.000	0.736-1.000	0.908-1.000	0.649-1.000	0.762 - 1.000
Theta range for data	$2.13^{\circ} < \theta < 30.00^{\circ}$	$1.21^\circ < \theta < 25.03^\circ$	$1.45^\circ < \theta < 23.26^\circ$	$1.69^\circ < \theta < 25.00^\circ$	$2.36^\circ < \theta < 24.98^\circ$
collection					
Reflections collected	62783	22658	19259	19720	15210
Unique reflections	$24062 (R_{int} = 0.0191)$	$11163 (R_{\rm int} = 0.0339)$	9068 ( $R_{\rm int} = 0.0483$ )	$37/1 (R_{\rm int} = 0.0468)$	$3645 (R_{\rm int} = 0.0254)$
No. of observed reflections $(I > 2\sigma_i)$	21741	10142	//36	3516	3209
No. of parameters	1132	923	904	230	228
Final $R_1$ , w $R_2$ values (I > $2\sigma_1$ )	0.0304, 0.0737	0.0527.0.1072	0.0772, 0.1448	0.0503, 0.1051	0.0315/0.0821
Final $R_1$ , w $R_2$ values (all data)	0.0347, 0.0759	0.0591. 0.1135	0.0937. 0.1535	0.0550, 0.1075	0.0368/0.0849
Residual electron density	+1.490, -0.913	+0.675, -0.442	+1.421, -0.817	+0.725, -1.053	+0.714, -0.744
peaks/e Å <sup>-3</sup>	,	,	. ,	,	,

Table 4Summary of crystallographic data for 1b, 2b, 3, 5a and 6a

values. The allyl ligand was found disordered in compounds **2b** and **3**. So as to model this disorder, in both cases the central carbon atom in the allyl ligand was split in two positions being only refined anisotropically at the part with site occupation factor > 0.5. In compounds **1b**, **2b** and **3** some CF<sub>3</sub> groups showed orientation disorder and were refined with 3 anisotropic major and 3 isotropic minor sites (no geometric restraints) with complementary site occupation factors. For compound **1b** dichloromethane solvate was refined in population parameter. The program ORTEP-3<sup>25</sup> was used for plotting.

## **Oligomerization reactions**

General procedure using cationic catalyst precursors. A Schlenk tube was loaded with 0.01 mmol of the cationic catalyst precursor (1a-b, 2a-b, 3 or 4) and the appropriate solvent (dichloromethane or 1,2-dichloroethane, 4 mL). Then, 20 mmol of either styrene, 4-methylstyrene or  $\alpha$ -methylstyrene were added. Normally, a violent, exothermic reaction takes place in a few seconds, causing the mixture to boil. After stirring for 45 min, MeOH (5 ml) was added and the mixture exposed to air. Some reactions with  $\alpha$ -methylstyrene were carried out at 50 °C for a period of 24 h. These were also quenched by addition of MeOH (5 mL) and exposed to air. The volatiles were removed in vacuo. Then, the residue was extracted with dichloromethane and filtered through a plug of silica gel. The silica gel was washed with several portions of dichloromethane, and the washings combined with the filtrate. Removal of the solvent using a rotary evaporator first, and a vacuum pump afterwards afforded an oily mixture of styrene oligomers. The ratios of the different oligomers present in the mixture were established by gel permeation chromatography (GPC).

General procedure using neutral catalyst precursors. A Schlenk tube was loaded with 0.02 mmol of the neutral catalyst precursor (5a–b or 6a–b) and 0.02 mmol of NaBAr'<sub>4</sub>. Then, 40 mmol of either styrene, 4-methylstyrene or  $\alpha$ -methylstyrene were added, and after that, 4 mL of fluorobenzene were added to the vigorously stirred mixture. Normally, an exothermic reaction takes place in most cases, but not so violent as with the cationic catalyst precursors. After stirring for 45 min at 25 °C (exceptionally 16 h for the reaction of 6b with  $\alpha$ -methylstyrene), MeOH (5 ml) was added and the mixture exposed to air. The work-up for the isolation and characterization of the oligomers was as described above.

In all cases, the oligomerization reactions were contrasted against a blank consisting of a reaction mixture identical to the system under study, but with no catalyst added.

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