Oligomerization and regioselective hydrosilylation of styrenes catalyzed by cationic allyl nickel complexes bearing allylphosphine ligands†‡

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The complexes $[Ni(\eta^3\text{-}CH_2CHCH_2)Br(\kappa^1 P\text{-}PR_2CH_2CH{=}CH_2)]$ (R = Ph **1**, ^{i}Pr **2**) and $[Ni(\eta^3\text{-}CH_2C(R')CH_2)(\kappa^1 P\text{-}PR_2CH_2CH{=}CH_2)_2][BAr'_4]$ (R′ = H, R = Ph **4a**, R = ^{i}Pr **4b**; R′ = CH_3, R = Ph **5a**, R = ^{i}Pr **5b**; Ar′ = 3,5-$C_6H_3(CF_3)_2$) have been prepared and characterized. The X-ray crystal structures of **1**, **2** and **5b** have been determined. **4a–b** and **5a–b** are catalyst precursors for the oligomerization of $RC_6H_4CH{=}CH_2$ to oligostyrene (R = H) or oligo(4-methylstyrene) (R = CH_3) respectively, without the need of a co-catalyst such as methylalumoxane. The catalytic activities range from moderate to high. The oligomerization reactions are carried out in the temperature interval 25–40 °C in 1,2-dichloroethane, using an olefin/catalyst ratio equal to 200, yielding oligostyrenes with a high isotactic fraction content P_m, with M_n in the range 700–1900 Dalton, and polydispersities between 1.22 and 1.64. The cationic complexes **4a–b** and **5a–b** are also effective catalyst precursors for the hydrosilylation reactions of styrene or 4-methylstyrene with $PhSiH_3$ in 1,2-dichloroethane at 40 °C using an olefin/catalyst ratio equal to 100, leading selectively to $RC_6H_4CH(SiH_2Ph)CH_3$ (R = H, CH_3) in 50–79% yield.

Introduction

The role played by Ni^{II} complexes in the fields of catalytic olefin oligomerization and polymerization is now very well established.[1–3] The catalytic properties of Ni^{II} complexes can be modified and tuned by the use of suitable ligands.[1] The α-diimine systems developed by Brookhart and co-workers, used in combination with methylalumoxane (MAO) are among the most prominent examples of these catalyst.[3] On the other hand, SHOP (Shell higher olefin process)-type systems use hemilabile ligands containing P and O donor atoms, being capable of olefin oligomerization and polymerization without the need of an aluminium-containing chemical as co-catalyst.[4–7] Brookhart and co-workers have reported that the cationic allyl complex $[Ni(\eta^3\text{-}CH_2CHCH_2)(P^tBu_2CH_2COPh)]^+$ is active for the aluminium-free polymerization of ethylene and copolymerization of ethylene and methyl 10-undecenoate.[8] This system takes advantage of the hemilabile character of the P,O-donor phenacyldi-*tert*-butylphosphine for the stabilization of reactive 14-electron species. Coordinatively unsaturated cationic indenyl nickel complexes of the type $[Ni(Indenyl)(PPh_3)]^+$ generated *in situ* have been shown to catalyze the dimerization of ethylene,[9] oligo- and polymerization of styrene and norbornene[10,11] as well as the hydrosilylation of several olefins and ketones.[12,13] Phosphine scavenging by $[Ni(Indenyl)(PPh_3)]^+$ leads to the cationic bis(phosphine) species $[Ni(Indenyl)(PPh_3)_2]^+$ which are much less active.[14,15] In order to circumvent this deactivation pathway, a number of indenyl ligands functionalized with different tethered, hemilabile moieties such as amines[16–18] or pendant olefins[14] that can occupy the open site around the Ni center. We have recently shown the ability of cationic allyl and indenyl nickel complexes of the type $[Ni(\eta^3\text{-}CH_2C(R)CH_2)(P)_2]^+$ and $[Ni(2\text{-methylindenyl})(P)_2]^+$ ($(P)_2$ = $(PMe^iPr_2)_2$, $(PPh^iPr_2)_2$, 1,2-bis(diisopropylphosphino)ethane (dippe)) to serve as catalyst precursors for the polymerization of styrene, leading to essentially atactic polystyrenes of rather high molecular weights.[19] It had been previously shown that the addition of phosphine ligands to $[Ni(\eta^3\text{-}CH_2C(R)CH_2)(COD)]^+$ causes a dramatic increase in the catalytic activity towards styrene polymerization, which leads to low molecular weight polystyrenes with increased stereoregularities, as inferred from the change in the isotactic content P_m from 0.65 up to 0.90 in some cases.[20,21] This was attributed to the generation of active cationic monophosphine and diphosphine species $[Ni(\eta^3\text{-}CH_2C(R)CH_2)(P)_n]^+$ (n = 1, 2) *in situ*. The addition of either $SbPh_3$ or $AsPh_3$ to $[Ni(\eta^3\text{-}CH_2C(R)CH_2)(COD)]^+$ produces a similar effect, leading mainly to styrene oligomers.[22] It appears then that coordinatively unsaturated fragments of the type $[Ni(\eta^3\text{-}CH_2C(R)CH_2)(P)]^+$ or $[Ni(indenyl)(P)]^+$ exhibit catalytic properties superior to those of their bis(phosphine) analogues. In an attempt to produce monophosphine complexes $[Ni(\eta^3\text{-}CH_2C(R)CH_2)(P)]^+$ amenable to isolation, yet maintaining most of its catalytic abilities for olefin oligo/polymerization and hydrosilylation, we envisaged the use of allylphosphines $PR_2CH_2CH{=}CH_2$ (R = Ph, ^{i}Pr) as co-ligands. Similarly to the approach used by Zargarian and co-workers when they introduced a pendant hemilabile olefin ligand in their $[Ni(Indenyl)(PPh_3)]^+$ system,[14] the use of $PR_2CH_2CH{=}CH_2$ might also provide useful insights into the possible mechanisms of interaction between the olefin and the

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‡ Electronic supplementary information (ESI) available: X-Ray crystal structure of **3b**; relevant GPC/SEC chromatograms. See DOI: 10.1039/b705579j

[Ni(η^3-CH$_2$C(R)CH$_2$)(P)]$^+$ fragment. Allyldiphenylphosphine is known to act as a potentially P,C,C-hemilabile ligand in complexes, by π-coordination of the double bond of the allyl group to the metal. For instance, treatment of [CpRuCl(PPh$_3$)(κ^1*P*-PPh$_2$CH$_2$CH=CH$_2$)] with NaPF$_6$ in EtOH leads to [CpRu(PPh$_3$)-(κ^3*P,C,C*-PPh$_2$CH$_2$CH=CH$_2$)][PF$_6$].[23] The homologous Cp* derivative [Cp*Ru(PPh$_3$)(κ^3*P,C,C*-PPh$_2$CH$_2$CH=CH$_2$)][PF$_6$] has been prepared by Zn reduction of [{Cp*RuCl$_2$}$_n$] in acetonitrile in the presence of PPh$_2$CH$_2$CH=CH$_2$ and subsequent treatment with NaPF$_6$.[24] Some complexes containing κ^3*P,C,C*-PR$_2$CH$_2$CH=CH$_2$ (R = Ph, ^{i}Pr) ligands have been structurally characterized by single crystal X-ray diffraction.[24,25]

In this work we describe the preparation of neutral and cationic allyl and 2-methylallyl nickel complexes bearing the potentially hemilabile phosphine ligands PR$_2$CH$_2$CH=CH$_2$ (R = ^{i}Pr, Ph). Although the attempts to isolate [Ni(η^3-CH$_2$C(R)CH$_2$)(κ^3*P,C,C*-PR$_2$CH$_2$CH=CH$_2$)]$^+$ met little success, we have prepared and characterized cationic bis(phosphine) derivatives [Ni(η^3-CH$_2$C(R)CH$_2$)(κ^1*P*-PR$_2$CH$_2$CH=CH$_2$)$_2$]$^+$ which have been shown to be active catalyst precursors for the oligomerization of styrene and 4-methylstyrene with a significant degree of stereoregularity, as well as for the regioselective hydrosilylation reactions of these olefins with PhSiH$_3$.

Results and discussion

Preparation of the complexes

The neutral allyl derivatives [Ni(η^3-CH$_2$CHCH$_2$)Br(κ^1*P*-PR$_2$CH$_2$CH=CH$_2$)] (R = Ph **1**, ^{i}Pr **2**) were prepared by reaction of [Ni(COD)$_2$] with either allyl bromide or 3-bromo-2-methylpropene and the corresponding phosphine in diethyl ether, followed by recrystallisation from toluene–petroleum ether (Chart 1).

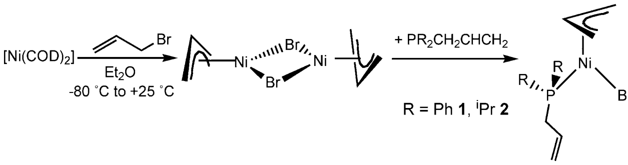


Chart 1

These complexes were isolated in the form of red crystalline solids, very air-sensitive in solution, where they decompose readily. Both **1** and **2** exhibit four very broad resonances in their ^{1}H NMR spectra attributable to the inequivalent *syn*- and *anti*- protons of the η^3-allyl ligand, whereas the ^{13}C{^{1}H} NMR spectra show three separate resonances for the carbon atoms of the η^3-allyl ligand. The chemical shift and splitting pattern of the ^{1}H and ^{13}C{^{1}H} NMR signals of the phosphine allyl substituent in **1** and **2** do not differ much from those corresponding to free PR$_2$CH$_2$CH=CH$_2$ (R = Ph, ^{i}Pr). This suggests that there is no significant interaction between the allylic double bond and the nickel atom. This has been confirmed by the determination of their respective X-ray crystal structures. ORTEP views of complexes **1** and **2** are respectively shown in Fig. 1 and 2, together with the most relevant bond distances and angles.

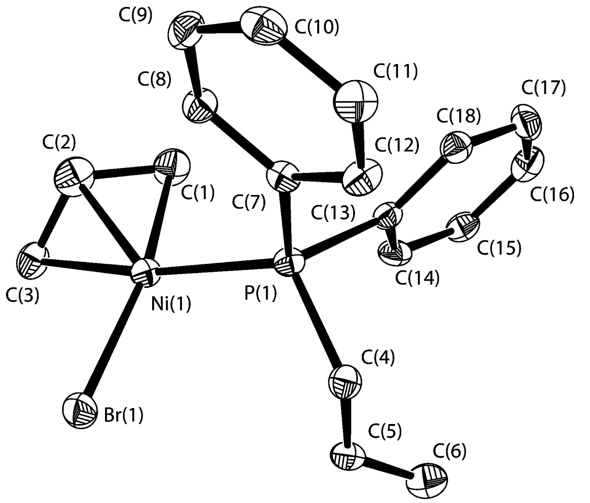


Fig. 1 ORTEP drawing (50% thermal ellipsoids) of the complex [Ni(η^3-CH$_2$CHCH$_2$)Br(κ^1*P*-PPh$_2$CH$_2$CH=CH$_2$)] (**1**). Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses: Ni(1)–C(1) 1.999(3); Ni(1)–C(2) 1.999(3); Ni(1)–C(3) 2.066(3); Ni(1)–P(1) 2.1941(10); Ni(1)–Br(1) 2.3224(7); C(1)–C(2) 1.415(5); C(2)–C(3) 1.366(5); C(4)–C(5) 1.489(4); C(5)–C(6) 1.313(5); Br(1)–Ni(1)–P(1) 97.77(2); C(1)–C(2)–C(3) 120.4(3).

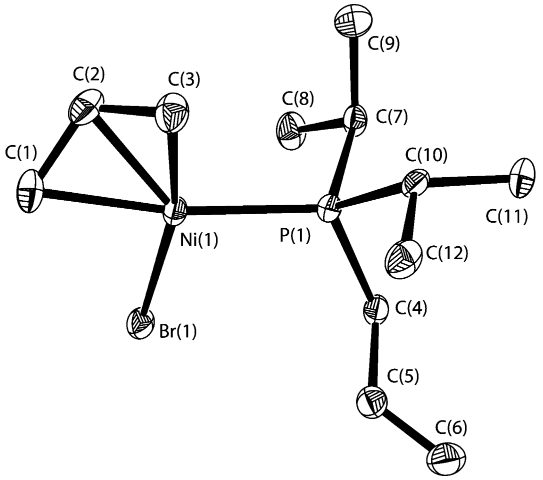


Fig. 2 ORTEP drawing (50% thermal ellipsoids) of the complex [Ni(η^3-CH$_2$CHCH$_2$)Br(κ^1*P*-P^{i}Pr$_2$CH$_2$CH=CH$_2$)] (**2**). Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses: Ni(1)–C(1) 2.057(4); Ni(1)–C(2) 1.998(4); Ni(1)–C(3) 1.998(4); Ni(1)–P(1) 2.1924(11); Ni(1)–Br(1) 2.3324(8); C(1)–C(2) 1.386(5); C(2)–C(3) 1.389(6); C(4)–C(5) 1.496(5); C(5)–C(6) 1.321(5); Br(1)–Ni(1)–P(1) 99.11(3); C(1)–C(2)–C(3) 118.8(4).

The crystal structures of complexes **1** and **2** consist of discrete molecules. The co-ordination geometry around nickel is pseudo-square-planar as expected for monomeric 16-electron η^3-allyl complexes. The double bond of the allylphosphine ligands points away from the metal, clearly indicating that there is no π-interaction at all with the nickel atom, as was already inferred from NMR spectroscopic data.

The sets of Ni–C, Ni–P and Ni–Br bond lengths for **1** and **2** are fully consistent with the data reported in the literature for related compounds, such as [Ni(η^3-CH$_2$CHCH$_2$)Br(PPh$_3$)],[26] [Ni(η^3-CH$_2$CHCHCH$_2$Ph)Br(PMe$_3$)],[27] and the dimer [{NiBr(P^{i}Pr$_3$)}$_2$(μ-η^3,η^3-(CH$_2$CHCH$_2$CH$_2$)$_2$].[28] The bond lengths C(1)–C(2) and C(2)–C(3) are not equal in the case of **1**, but they are almost identical in the case of **2**. The values are intermediate between single and double bonds, and compare well with data in the literature.[26–28] The angles formed by the least squares planes defined by the allyl ligands and the plane defined by the NiBrP moieties are 66.4(3)° for **1** and 65.9(3)° for **2**.

Attempts to isolate the homologous complexes of **1** and **2** bearing a η^3-methylallyl ligand instead of η^3-allyl were unsuccessful. Although the course of the reactions of $[Ni(COD)_2]$ with 2-methyl-1-bromopropene and the allylphosphines seems to be the same as for the preparation of **1** or **2**, upon work-up no η^3-methylallyl derivatives were isolated. Instead, dark red or purple crystalline materials, identified as $[NiBr_2(\kappa^1 P\text{-}PR_2CH_2CH{=}CH_2)_2]$ (R = Ph **3a**, ^{i}Pr **3b**) were obtained. The X-ray crystal structure of **3b** as well as comments on the NMR spectral properties of these complexes are supplied as part of the electronic supplementary information (ESI‡). We had previously reported the preparation of the related dibromo complexes $[NiBr_2(PR^iPr_2)_2]$ (R = Me, Ph). These compounds were recovered from the reaction mixtures with Li(2-methylindenyl) during attempts made to prepare the derivatives $[Ni(2\text{-methylindenyl})Br(PR^iPr_2)]$.[19] We suggested that presumably $[Ni(2\text{-methylindenyl})Br(PR^iPr_2)]$ are unstable and undergo redistribution reactions, leading to the starting dibromo complexes plus $[Ni(2\text{-methylindenyl})_2]$. It is likely that in the course of the preparation of the neutral η^3-methylallyl derivatives with $PR_2CH_2CH{=}CH_2$ reductive coupling of the allyl moieties occurs in the presence of the phosphine ligands, although this issue was not investigated any further.

We carried out bromide abstraction reactions from **1** and **2** in an attempt to prepare cationic derivatives in which the double bond of the phosphine allyl substituent might fill the vacant position left by bromide (*i. e.*, $\kappa^3 P,C,C\text{-}PR_2CH_2CH{=}CH_2$). Upon addition of $NaBAr'_4$ to a fluorobenzene solution of either **1** or **2**, a yellow solution and a finely divided black precipitate was formed almost immediately. The black precipitate suggests the reduction of Ni^{II} to Ni^0. The work-up of the solutions led to the isolation of the cationic allylbis(phosphine) complexes $[Ni(\eta^3\text{-}CH_2CHCH_2)(\kappa^1 P\text{-}PR_2CH_2CH{=}CH_2)_2][BAr'_4]$ (R = Ph **4a**, ^{i}Pr **5a**). Hence, the halide abstraction reaction takes place with partial decomposition. Apparently, the monophosphine species generated *in situ* upon bromide removal, either $[Ni(\eta^3\text{-}CH_2CHCH_2)(\kappa^3 P,C,C\text{-}PR_2CH_2CH{=}CH_2)][BAr'_4]$ or the even more reactive $[Ni(\eta^3\text{-}CH_2CHCH_2)(\kappa^1 P\text{-}PR_2CH_2CH{=}CH_2)][BAr'_4]$ have a very strong tendency for adding an extra phosphine ligand. Rather than filling the gap generated by bromide abstraction with the coordination of the double bond of the phosphine allyl substituent as intended, these species readily scavenge $PR_2CH_2CH{=}CH_2$ from another complex present in the mixture (most likely **1** or **2**) furnishing the corresponding bis(phosphine) derivatives accompanied by decomposition products (Chart 2). The fate of the allyl ligands during the decomposition process was not investigated in detail.

The yield of **4a** and **5a** from these reactions was below 50% as expected, since the starting neutral monophosphine complexes **1** or **2** were the only source for $PR_2CH_2CH{=}CH_2$. These compounds were more conveniently prepared in higher yields by reaction of $[\{Ni(\eta^3\text{-}CH_2CHCH_2)(\mu\text{-}Br)\}_2]$ (generated *in situ* by reaction of $[Ni(COD)_2]$ with allyl bromide) with two equivalents of $PR_2CH_2CH{=}CH_2$ in diethyl ether, followed by subsequent treatment with $NaBAr'_4$. The methylallyl derivatives $[Ni(\eta^3\text{-}CH_2C(CH_3)CH_2)(\kappa^1 P\text{-}PR_2CH_2CH{=}CH_2)_2][BAr'_4]$ (R = Ph **4b**, ^{i}Pr **5b**) were synthesized by following an analogous procedure, replacing allyl bromide by 2-methyl-1-bromopropene. The X-ray crystal structure of **5b** was determined. An ORTEP view of the complex cation in **5b** is shown in Fig. 3.

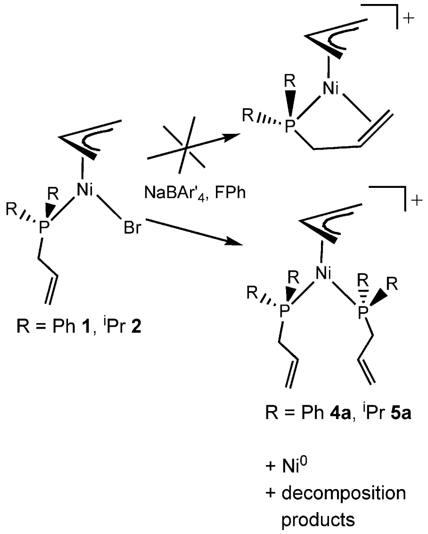


Chart 2

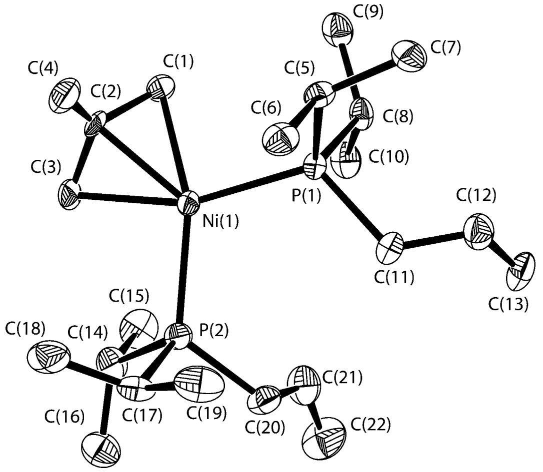


Fig. 3 ORTEP drawing (50% thermal ellipsoids) of the complex cation $[Ni(\eta^3\text{-}CH_2C(CH_3)CH_2)(\kappa^1 P\text{-}P^iPr_2CH_2CH{=}CH_2)_2]^+$ in **5b**. Hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses: Ni(1)–C(1) 2.049(4); Ni(1)–C(2) 2.040(4); Ni(1)–C(3) 2.047(4); Ni(1)–P(1) 2.2215(13); Ni(1)–P(2) 2.2386(13); C(1)–C(2) 1.399(6); C(2)–C(3) 1.396(7); C(2)–C(4) 1.499(7); C(11)–C(12) 1.489(6); C(12)–C(13) 1.310(7); C(20)–C(21) 1.475(7); C(21)–C(22) 1.311(8); P(1)–Ni(1)–P(2) 110.61(5); C(1)–C(2)–C(3) 116.2(5); torsion angle C(11)– P(1)– P(2)–C(20) 21.4(2).

The complex cation in **5b** has a pseudo-square-planar structure, very similar to those of the related complexes $[Ni(\eta^3\text{-}CH_2C(CH_3)CH_2)(P^iPr_2Ph)_2]^+$,[19] $[Ni(\eta^3\text{-}CH_2CHCH_2)(PPh_3)_2]^+$,[14] and $[Ni(\eta^3\text{-}C(CH_3)_2C(CH_3)CH_2)(PPh_3)_2]^+$.[29] The Ni–C and Ni–P separations suggest a fairly symmetrical arrangement of the phosphines and the allyl ligand, consistent with the essentially identical C(1)–C(2) and C(2)–C(3) bond lengths in the allyl ligand. The Ni–P bond distances are slightly longer than those observed for the neutral complexes **1** and **2**, but shorter than in

$[Ni(\eta^3\text{-}CH_2C(CH_3)CH_2)(P^iPr_2Ph)_2]^+$.[19] The double bonds of the phosphine allyl substituents point away from the nickel atom, and no close contact between nickel and any of these carbon atoms has been detected. The dihedral angle between planes C(11)–P(1)–P(2) and P(1)–P(2)–C(20) is 21.4(3)°, which indicates an almost eclipsed conformation of the $P^iPr_2CH_2CH{=}CH_2$ ligands with respect to each other, whereas the angle formed by the least squares planes defined by the allyl ligand and the plane defined by the NiP_2 moiety is 67.6(3)°.

Although we did not succeed in the isolation of cationic complexes of the type $[Ni(\eta^3\text{-}CH_2C(R)CH_2)(\kappa^3 P,C,C\text{-}PR'_2CH_2CH{=}CH_2)]^+$ containing one allylphosphine ligand acting in a hemilabile fashion, the 16-electron cationic bis(phosphine) complexes **4a–b** and **5a–b** have been shown to be active catalyst precursors for the oligomerization of styrene and 4-methylstyrene, as well as for the hydrosilylation reactions of these olefins with $PhSiH_3$.

Oligomerization reactions

The cationic allyl and methylallyl derivatives **4a–b** and **5a–b** are catalytic precursors for the oligomerization of styrene or 4-methylstyrene in the absence of a co-catalyst such as MAO. The best results were obtained using as solvent 1,2-dichloroethane at a temperature of 40 °C, with a monomer/catalyst molar ratio equal to 200 under a dinitrogen atmosphere. The amounts of oligostyrene or oligo(4-methylstyrene) increase steadily with reaction time. After 1 h at 40 °C the conversion of the olefin into oligomers is almost complete in most cases. When **4b** is used as catalyst, the oligomerization reaction is very fast and exothermic, causing the mixture to boil even though no external source of heat is applied. In this case, the conversion is complete in far less than 5 min. The oligomerization reactions of 4-methylstyrene are in general slower, although when **4b** is used as catalyst the oligomerization is as fast and exothermic as in the case of the reaction with styrene. With the sole exception of the reactions catalyzed by **4b**, the oligostyrene or oligo(4-methylstyrene) yields drop rapidly when the temperature is lowered. Periods of time of 5 h or longer are necessary to achieve significant conversions when the reactions are performed at 25 °C. The individual yields of oligostyrene or oligo(4-methylstyrene) obtained using each of the catalysts after the appropriate reaction times and the resulting turnover frequency (N_t)[30] are listed in Table 1.

Examination of the values of N_t indicate that the methylallyl complexes are significantly more active that their counterparts bearing allyl. On the other hand, the systems containing

Table 1 Oligomerization of styrene catalyzed by complexes **4a–b** and **5a–b**

							Oligomer[c]				
Entry[a]	Catalyst	Olefin	$T/°C$	t/h	Yield (%)	$N_t{}^b/h^{-1}$	P_m	M_w	M_n	M_w/M_n	Distribution weight[d] (%)
1	**4a**	Styrene	40	0.5	26	103	nd[e]	1008	808	1.25	86
								342	336	1.02	11
								218	215	1.01	3
2	**4a**	Styrene	40	1	94	187	0.79	985	799	1.23	84
								345	340	1.01	12
								223	220	1.01	4
3	**4a**	Styrene	15	24	80	7	0.66	17653	9841	1.79	41
								1059	813	1.30	47
								305	301	1.01	10
								191	188	1.02	2
4	**4b**	Styrene	25	<0.08	100	>2486	0.78	937	765	1.22	81
								343	337	1.02	15
								217	214	1.01	4
5	**5b**	Styrene	40	1	70	139	0.85	1678	1128	1.49	95
								340	336	1.01	4
								212	208	1.02	1
6	**5b**	Styrene	40	1	95	189	0.84	1472	1030	1.43	91
								331	326	1.01	7
								223	221	1.01	2
7	**4a**	Styrene	25	15	70	9	0.84	27028	17903	1.51	6
								1660	1073	1.55	93
8	**4b**	4-Methyl- styrene	40	20	100	10	0.83	1453	1089	1.33	90
								403	398	1.01	7
								256	250	1.02	3
9	**5a**	4-Methyl- styrene	25	<0.08	100	>2486	0.76	1263	999	1.26	86
								410	403	1.02	10
								253	247	1.02	4
10	**5b**	4-Methyl- styrene	40	5	40	16	0.85	2814	1844	1.53	100
11	**5b**	4-Methyl- styrene	40	1	100	199	0.83	2057	1344	1.54	97
								300	293	1.02	3
12	**4b**	4-Methyl- styrene	25	22	100	9	0.85	2456	1501	1.64	98
								270	262	1.03	2

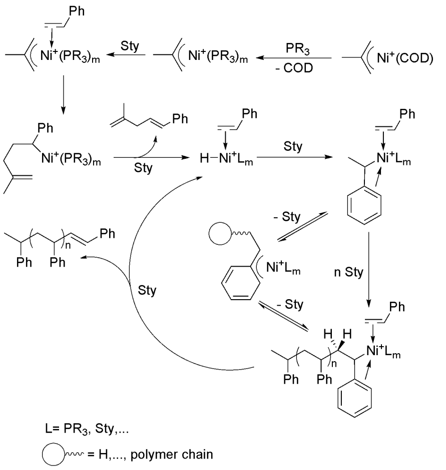
[a] Experimental conditions: substrate (1 g), solvent:1,2-dichloroethane (1 mL), [olefin]/[Ni]= 200. [b] N_t = (moles of converted styrene or 4-methylstyrene)/[(moles of catalyst) × time]. [c] Determined by GPC/SEC. [d] Estimated by area integration of the distribution peaks in the GPC/SEC chromatogram. [e] nd = not determined.

$PPh_2CH_2CH{=}CH_2$ are in general more active that those with $P^iPr_2CH_2CH{=}CH_2$, but the differences are not as remarkable as those attributable to the presence of one methyl substituent on the allyl ligand.

The oligostyrenes obtained in these catalytic reactions were characterized by GPC/SEC and their mass features, at the end of the oligomerization reaction, are listed in Table 1. For the reactions performed at 40 °C, and also for the reactions catalyzed by **4b**, the GPC traces indicate rather narrow molecular weight distributions, which can be treated as multimodal: one main peak (80–100%) corresponding to oligostyrene or oligo(4-methylstyrene), and two small peaks (summing to less than 20%) attributable respectively to the trimers and dimers of styrene or 4-methylstyrene. In a few cases the amounts of trimer and dimer were negligible and the molecular weight distributions were treated as unimodal. The values of M_n range from 700 to 1900 Dalton for the main peak of the distributions, with polydispersity indexes (M_w/M_n) in the range 1.22–1.64. In the cases in which the reactions were performed at temperatures of 25 °C or below (with exception of those in which catalyst **4b** was used), a higher molecular weight distribution peak was observed in addition to those present in the GPC traces of the oligomerization runs performed at 40 °C. This peak accounts for the 41% of the distribution weight in the case of the oligostyrene obtained in the reaction catalyzed by **4a** at 15 °C, and has a M_n value of 9841 Dalton and a polydispersity index of 1.79 (entry 3). A similar peak having a M_n value of 17903 Dalton and a polydispersity index of 1.51 is present in the oligostyrene resulting from the reaction catalyzed by **5b** at 25 °C, but in this case this peak represents only 6% of the total distribution weight (entry 7). The observed values of M_n for the main peak in the GPC traces depend essentially on the substituents present on the phosphine ligand. Thus, the reactions catalyzed by complexes containing $PPh_2CH_2CH{=}CH_2$ led always to oligomers with M_n values lower than in the case of oligomers resulting from reactions catalyzed by complexes bearing $P^iPr_2CH_2CH{=}CH_2$. The values of M_n of 799–765 are consistent with chains of 7–8 styrene units (*i.e.* C_{14}–C_{16}) in the case of catalysis with **4a–b** (entries 1–4), whereas for the reactions catalyzed by complexes **5a–b** (entries 5–7) the values of M_n between 1073 and 1128 suggest longer chains, of 9–10 styrene units (C_{18}–C_{20}). The oligomers derived from 4-methylstyrene have slightly longer carbon chains than in the case of oligostyrenes: between 8 and 10 monomer units for the reactions catalyzed by **4a–b** (entries 8,9), and between 11 and 16 for the reactions catalyzed by **5a–b** (entries 10–12). The values of M_n are rather indifferent to the presence of either allyl or methylallyl in the catalyst precursors.

The variation of M_n with the conversion into oligostyrene suggests that the oligomerization processes hereby considered are clearly not living. We have monitored the variation of M_n as a function of the oligostyrene yield for the reaction catalyzed by **4a**. M_n increases initially with conversion to a value which, after that, remains stable when the conversion increases. The values of M_n measured for the oligomers obtained in the reactions catalyzed by **5a–b** at low conversion figures are essentially identical to those measured at the end of the processes.

The oligostyrenes obtained in the catalytic runs were also characterized by means of ^1H and $^{13}C\{^1H\}$ NMR spectroscopy (1,1,2,2-tetrachloroethane-d_2, 120 °C). According to the literature, the analysis of the intensity distribution of the $^{13}C\{^1H\}$ NMR resonances corresponding to the *ipso*-carbon atoms of the phenyl groups of polystyrene gives information relevant to the tacticity of polystyrenes.[19,20,21] The isotactic contents, P_m, calculated from the analysis of the intensity distribution of the $^{13}C\{^1H\}$ NMR resonances corresponding to the *ipso*-carbon atoms of the phenyl groups for the oligomers obtained in this work fall in the range 0.76 to 0.85 (with the exception of entry 3 in Table 1). It can be concluded that the oligostyrenes resulting from the catalytic reactions under study have high isotactic content, and hence any possible mechanism for the oligomerization reaction must account for the observed stereoregularity. In our case, both the M_n and the P_m values are similar to those observed for the oligostyrenes resulting from the reactions catalyzed by the system $[Ni(\eta^3\text{-}CH_2C(CH_3)CH_2)(COD)]^+/PR_3$ ($PR_3 = PPh_3$, $P(OPh_3)$, $P(o\text{-}Tol)_3$, PMe_3, P^nBu_3, PCy_3).[20,21] For this system, an insertion mechanism was proposed involving addition of styrene to a Ni–H bond to yield a styryl complex, bound to the nickel center in an η^3-benzylic fashion, which by multiple insertion and subsequent β-hydride elimination gives rise to regioregular head-to-tail polystyrene chains containing methyl and unsaturated end-groups (Scheme 1).

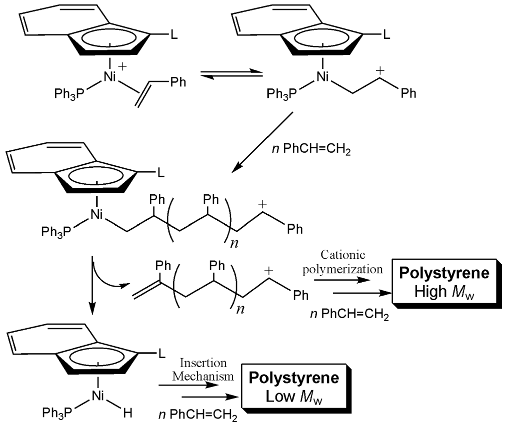


Scheme 1

Alternatively, Zargarian and co-workers have suggested a Ni-initiated electrophilic route for the styrene polymerization mediated by $[Ni(1\text{-}L\text{-}Indenyl)(PPh_3)]^+$ ($L = CH_2CH_2CH{=}CH_2$, $SiPh_2CH_2CH{=}CH_2$, Scheme 2), involving the formation of a polymer chain-centered carbocation.[14]

The polymer chain grows *via* nucleophilic attack of styrene, until it undergoes β-elimination to give a Ni–H species and a carbocation-terminated polymer chain. The latter continues growing *via* an electrophilic mechanism (cationic polymerization) leading to polystyrene with high molecular weight. The nickel hydride could then initiate a different polymerization process *via* an insertion mechanism similar to that outlined above, leading to low molecular weight oligo- or polystyrenes.[14]

Given the similarities between the molecular weight distributions and the isotactic contents of the oligomers obtained in our systems and those of the $[Ni(\eta^3\text{-}CH_2C(CH_3)CH_2)(COD)]^+/PR_3$ system,[20,21] it seems logical to assume that the mechanism in our case is analogous to that shown in Scheme 1. However, at low temperatures a second mechanism, competing with the insertion mechanism could be at work, as inferred from the bimodal, higher



Scheme 2

Table 2 Hydrosilylation reactions of styrene or 4-methylstyrene with $PhSiH_3$ catalyzed by complexes **4a–b** and **5a–b**[a]

Entry	Catalyst	Olefin	Yield[b] (%)
1	**4a**	Styrene	74
2	**4b**	Styrene	47
3	**5a**	Styrene	79
4	**5b**	Styrene	68
5	**4a**	4-Methylstyrene	50
6	**4b**	4-Methylstyrene	40
7	**5a**	4-Methylstyrene	60
8	**5b**	4-Methylstyrene	70

[a] Experimental conditions: olefin (1 mmol), $PhSiH_3$ (2 mmol), solvent: 1,2-dichloroethane (0.25 mL), temperature: 40 °C, [olefin]/[Ni] = 100. [b] Calculated as: [mmol of $RC_6H_4CH(SiH_2Ph)CH_3$ obtained/mmol of $RC_6H_4CH{=}CH_2$] × 100 (R = H, CH_3).

molecular weight distributions and the lower isotactic content of the polymers obtained under these conditions (*i.e.* entry 3, Table 1). This could be a cationic mechanism similar to that shown in Scheme 2. In our previous report on styrene polymerization by cationic allyl and 2-methylindenyl nickel phosphine complexes we also pointed out that two mechanisms were operative, one of them being presumably of the insertion type, but the mechanism responsible for the bulk of the polystyrenes obtained during the reactions was either cationic or even free-radical, accounting for the observed high molecular weights and their low isotactic contents (essentially atactic polystyrenes).[19]

In order to gather some additional information on the possible oligomerization mechanism, we performed an NMR experiment in which we monitored the reaction of **4a** with *ca.* 10 equivalents of styrene in CD_2Cl_2 at 35 °C. Consumption of styrene and formation of oligostyrene was observed in the ^1H NMR, but there was no decrease in the intensity of the Ni–allyl or phosphine resonances. Consistent with this, the $^{31}P\{^1H\}$ NMR showed one singlet at the position expected for **4a**. These observations suggest that only a small fraction of the catalyst precursor is initiated, followed by rapid propagation and chain growth. This sort of behavior has been also observed in ethylene polymerization catalyzed by $[Ni(\eta^3\text{-}CH_2CHCH_2)(^tBu_2PCH_2COPh)][BAr'_4]$.[8]

Hydrosilylation reactions

The cationic complexes **4a–b** and **5a–b** act as catalyst precursors for the regioselective hydrosilylation reactions of styrene or 4-methylstyrene with $PhSiH_3$. These reactions have been carried out using a 1% mol catalyst load in 1,2-dichloroethane at 40 °C. Under these conditions, the hydrosilylation products isolated upon purification were either $C_6H_5CH(CH_3)SiH_2C_6H_5$ or $CH_3C_6H_4CH(CH_3)SiH_2C_6H_5$, resulting from the reaction of $PhSiH_3$ with styrene or with 4-methylstyrene respectively. The amounts of the β-isomers $RC_6H_5CH_2CH_2SiH_2C_6H_5$ if present, were absolutely negligible. The yields of isolated hydrosilylation products after 5 h were in the range 50–79%. The corresponding figures for each catalyst and olefin are listed in Table 2.

These results compare well in terms of activity and regioselectivity with those reported by Zargarian and co-workers using substituted indenyl nickel complexes as catalyst precursors, although no activator (*i.e.* MAO, or $NaBPh_4$) is needed in our case.[12,14] Furthermore, very low activity for hydrosilylation has been reported for the cationic bis(phosphine) complex $[Ni(1\text{-}Methylindenyl)(PPh_3)_2][BPh_4]$,[14] a result which is in sharp contrast with the reactivity of our systems. Studies on the dehydrooligomerization of $PhSiH_3$ catalyzed by $[Ni(1\text{-}Methylindenyl)(CH_3)(PR_3)]$ (R = Ph, Cy, Me) have led to the proposal of a catalytic cycle which involves the formation of nickel silyl and hydrido species as intermediates.[31] For the hydrosilylation of styrene a nickel hydride species has also been invoked as the active intermediate in these reactions. In the case of cationic species, the Ni–H should be generated *via* the transfer of hydride from $PhSiH_3$ to the highly electrophilic $[Ni(1\text{-}Methylindenyl)(PR_3)]^+$ fragment, leaving a $[PhSiH_2]^+$ which might be trapped by free PR_3 furnishing $[R_3P\text{-}SiH_2Ph]^+$. However, it was not possible to obtain direct NMR spectroscopic evidence for the formation of a Ni–H bond, although free phosphine was detected in the early stages of the catalytic cyle.[12,14]

We have monitored by NMR spectroscopy the reaction of **4b** with *ca.* 10 equivalents of $PhSiH_3$ in CD_2Cl_2 at 35 °C first, and then with styrene (*ca.* 10 equivalents). Fig. 4 shows the $^{31}P\{^1H\}$ NMR spectra at different stages of this process.

Shortly after the addition of $PhSiH_3$, two sets of resonances corresponding to AB spin systems (two doublets each set, J_{PP} = 19 Hz) begin to appear in the $^{31}P\{^1H\}$ NMR spectrum. After 10 min, the intensity of the doublets has increased at the expense of the intensity of the singlet of **4b**, and a new singlet begins to arise at 20.4 ppm. After 15 min, the intensities of the doublets decrease as the intensity of the new singlet at 20.4 ppm increases. At this point, the ^1H NMR reveals the formation of the dimer $(PhSiH_2)_2$ (singlet at 4.60 ppm) and the disappearance of the resonances attributable to **4b**, being replaced by rather uninformative complex multiplet signals. No hydride resonances were present. When styrene was added, the formation of $PhCH(CH_3)SiH_2Ph$ was detected shortly afterwards by ^1H NMR spectroscopy, but no further changes occur in the $^{31}P\{^1H\}$ NMR. These data clearly indicate that there is no phosphine dissociation in our system under study, since no signals attributable to free $PPh_2CH_2CH{=}CH_2$ were detected. Furthermore, the observation of resonances corresponding to AB spin systems upon addition of $PhSiH_3$ indicate that the two phosphorus atoms remain bonded to the metal, and that they become inequivalent. The values of 19 Hz for the J_{PP} coupling constants are consistent with a *cis*-arrangement of the phosphorus atoms, hence their inequivalence must arise from changes in the

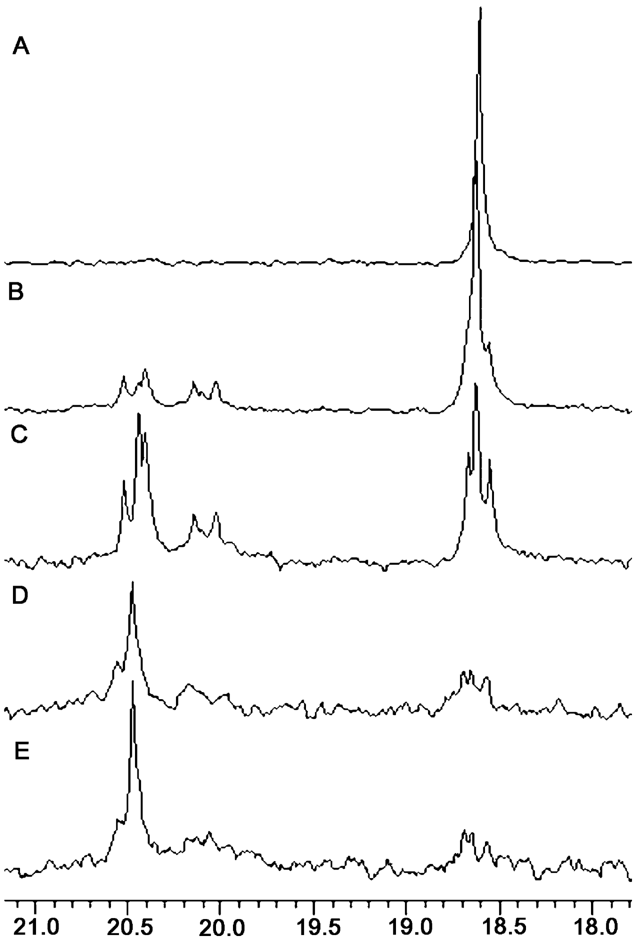


Fig. 4 $^{31}P\{^1H\}$ NMR spectra (CD_2Cl_2, 35 °C) of: (a) **4b**; (b) **4b** plus $PhSiH_3$ after 5 min, (c) **4b** plus $PhSiH_3$ after 10 min, (d) **4b** plus $PhSiH_3$ after 15 min, (e) 10 min after addition of styrene to (d).

ligands in a *trans*-position with respect to these phosphorus atoms, although the hydrosilylation of the double bond of the phosphine allyl substituent can not be disregarded. After a brief period of time, the phosphorus atoms become equivalent again, and the new singlet resonance at 20.4 ppm in the $^{31}P\{^1H\}$ NMR might be attributed to the catalytically active species for the hydrosilylation process. Although these data are insufficient to support a detailed mechanistic proposal, they point to an initial activation process of the pre-catalyst by reaction with $PhSiH_3$ which does not involve phosphine dissociation, to yield the catalytically active species. Since Si–H bond activation takes place during the process, the participation of nickel silyl and hydrido species is assumed, as suggested by Zargarian and co-workers,[12,14,31] but little can be said about the nature of such species. Further work might shed new information on the catalytically active species, as well as expand the scope of applicability of these hydrosilylation reactions.

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 ligand diphenylallylphosphine was purchased from Aldrich, whereas diisopropylallylphosphine was obtained by reaction of PCl^iPr_2 with one equivalent of allylmagnesium chloride in diethyl ether. The complex $[Ni(COD)_2]$ was obtained according to the literature.[32] Styrene was purified by treatment with CaH_2 followed by trap-to-trap distillation. NMR spectra were taken on Varian Inova 400 MHz or Varian Gemini 300 MHz equipment. Chemical shifts are given in ppm from $SiMe_4$ (^1H and $^{13}C\{^1H\}$), or 85% H_3PO_4 ($^{31}P\{^1H\}$). 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 × 300 mm). The oligomer samples were eluted with THF at a flow rate of 1 $cm^3\ min^{-1}$. The system was calibrated using a Merck polystyrene standard kit.

$[Ni(\eta^3\text{-}CH_2CHCH_2)Br(\kappa^1P\text{-}PPh_2CH_2CH{=}CH_2)]$ (1)

To a slurry of $[Ni(COD)_2]$ (0.54 g, 2 mmol) in diethyl ether (20 mL) cooled in a liquid N_2–ethanol bath, allyl bromide (173 µL, 2 mmol) was added. The mixture was warmed to room temperature and stirred for 1 h. During this time, the color of the mixture changed from yellow to red. At this stage diphenylallylphosphine (0.44 mL, 2 mmol) was added. The mixture was stirred for 15 min. The color of the solution became dark red. The solvent was removed *in vacuo*, and the resulting solids were dissolved in toluene. The solution was filtered, layered with petroleum ether and cooled to −20 °C. Red crystals were obtained, which were separated from the mother liquor by decantation and dried under an argon stream. Yield: 0.59 g, 74%. Anal. Calcd for $C_{18}H_{20}BrNiP$: C, 53.3; H, 4.97. Found: C, 53.4; H, 4.99%. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 1.90, 2.85 (s br, 1 H each, $CH^{syn}H^{anti}CHCH^{syn}H^{anti}$), 2.95, 4.10 (s br, 1 H each, $CH^{syn}H^{anti}CHCH^{syn}H^{anti}$), 3.24 (m, 2 H, $Ph_2PCH_2CH{=}CH_2$), 4.91, 5.01 (d br, 1 H each, $Ph_2PCH_2CH{=}CH_2$), 5.34 (m, 1 H, CH_2CHCH_2), 5.87 (m, 1 H, $Ph_2PCH_2CH = CH_2$), 7.43, 7.57 (m, 10 H, PC_6H_5); $^{31}P\{^1H\}$ NMR (161.89 MHz, CD_2Cl_2, 298 K): δ 20.26 (s); $^{13}C\{^1H\}$ NMR (100.57 MHz, CD_2Cl_2, 298 K): δ 33.5 (d, J_{CP} = 23.5 Hz, $Ph_2PCH_2CH{=}CH_2$), 54.1, 72.8 (br, CH_2CHCH_2), 110.2 (s, CH_2CHCH_2), 119.38 (d, J_{CP} = 9.75 Hz, $Ph_2PCH_2CH = CH_2$), 130.9 (s, $Ph_2PCH_2CH{=}CH_2$), 128.6, 130.4, 133.1 (s, PC_6H_5).

$[Ni(\eta^3\text{-}CH_2CHCH_2)Br(\kappa^1P\text{-}P^iPr_2CH_2CH{=}CH_2)]$ (2)

This compound was obtained by a procedure analogous for that used for **1**, using $P^iPr_2CH_2CH{=}CH_2$ (0.3 mL, 2 mmol) instead of $PPh_2CH_2CH{=}CH_2$. Yield: 0.61 g, 65%. Anal. Calcd for $C_{12}H_{24}BrNiP$: C, 42.7; H, 7.16. Found: C, 42.4; H, 7.09%. ^1H NMR (400 MHz, C_6D_6, 298 K) δ 0.92, 1.06 (br, 12 H, $PCH(CH_3)_2$), 1.32, 2.42 (br, 1 H each, $CH^{syn}H^{anti}CHCH^{syn}H^{anti}$), 1.78 (m br, 2 H, $PCH(CH_3)_2$), 2.42 (br, 2 H, $^iPr_2PCH_2CH{=}CH_2$), 2.92, 4.19 (br, 1 H each, $CH^{syn}H^{anti}CHCH^{syn}H^{anti}$), 4.91, 4.95 (br, 2 H, $^iPr_2PCH_2CH{=}CH_2$), 4.74 (br, 1 H, CH_2CHCH_2), 5.87 (br, 1 H, $^iPr_2PCH_2CH = CH_2$). $^{31}P\{^1H\}$ NMR (161.89 MHz, C_6D_6, 298 K) δ 32.7 (s); $^{13}C\{^1H\}$ NMR (100.57 MHz, C_6D_6, 298 K): δ 18.3, 19.34 (br, $PCH(CH_3)_2$), 24.4 (d, J_{CP} = 21.2 Hz, $PCH(CH_3)_2$), 27.9 (d, J_{CP} = 19.51 Hz, $^{i}\mathrm{Pr_2P}\mathit{C}\mathrm{H_2CH{=}CH_2}$), 47.2, 74.5 (br, $\mathit{C}\mathrm{H_2CH}\mathit{C}\mathrm{H_2}$), 108.4 (s, $\mathrm{CH_2}\mathit{C}\mathrm{HCH_2}$), 117.5 (d, J_{CP} = 9.8 Hz, $^{i}\mathrm{Pr_2PCH_2CH} = \mathit{C}\mathrm{H_2}$), 133.5 (s, $^{i}\mathrm{Pr_2PCH_2}\mathit{C}\mathrm{H{=}CH_2}$).

trans-$[\mathrm{NiBr_2(\kappa^1}\mathit{P}\text{-}\mathrm{PR_2CH_2CH{=}CH_2)_2}]$ (R = Ph 3a, ^{i}Pr 3b)

To a slurry of anhydrous $\mathrm{NiBr_2}$ (0.22 g, 1 mmol) in ethanol (20 mL), either $\mathrm{PPh_2CH_2CH{=}CH_2}$ (0.44 mL, 2 mmol) or $\mathrm{P^iPr_2CH_2CH{=}CH_2}$ (0.30 mL, 2 mmol) was added. The color immediately changed to dark red (**3a**) or dark purple (**3b**) with precipitation of a crystalline material. The reaction mixture was stirred at room temperature for 30 min. The resulting crystalline precipitate was filtered off, washed with ethanol and petroleum ether, and dried under vacuum.

Data for 3a. Yield: 0.57 g, 85%. Anal. Calcd for $\mathrm{C_{30}H_{30}Br_2NiP_2}$: C, 53.7; H, 4.51. Found: C, 53.9; H, 4.69%. ^{1}H NMR (400 MHz, $\mathrm{CD_2Cl_2}$, 193 K) δ 3.12 (br, 4 H, $\mathrm{Ph_2PC}\mathit{H}_2\mathrm{CH{=}CH_2}$), 4.95 (br, 4 H, $\mathrm{Ph_2PCH_2CH{=}C}\mathit{H}_2$), 5.90 (br, 2 H, $\mathrm{Ph_2PCH_2C}\mathit{H} = \mathrm{CH_2}$), 7.60 (br, 20 H, $\mathrm{C_6}\mathit{H}_5$); ^{31}P{^{1}H} NMR (161.89 MHz, $\mathrm{CD_2Cl_2}$, 193 K): δ 6.48 (s); ^{13}C{^{1}H} NMR not recorded.

Data for 3b. Yield: 0.49 g, 92%. Anal. Calcd for $\mathrm{C_{18}H_{38}Br_2NiP_2}$: C, 40.4; H, 7.17. Found: C, 40.6; H, 7.34%. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$, 298 K): δ 1.19 (d, J_{HH} = 6.8 Hz, 6 H, $\mathrm{PCH(C}\mathit{H}_3\mathrm{)_2}$), 1.56 (d, J_{HH} = 7.2 Hz, 6 H, $\mathrm{PCH(C}\mathit{H}_3\mathrm{)_2}$), 2.72 (m, 4 H, $\mathrm{PC}\mathit{H}\mathrm{(CH_3)_2}$), 2.64 (d, 4 H, $\mathrm{Ph_2PC}\mathit{H}_2\mathrm{CH{=}CH_2}$), 4.99, 5.03 (d, 2 H each, $^{i}\mathrm{Pr_2PCH_2CH{=}C}\mathit{H}_2$), 6.42 (m, 2 H, $^{i}\mathrm{Pr_2PCH_2C}\mathit{H} = \mathrm{CH_2}$); ^{31}P{^{1}H} NMR (161.89 MHz, $\mathrm{CD_3COCD_3}$, 213 K): δ 16.97 (s); ^{13}C{^{1}H} NMR (75.4 MHz, $\mathrm{CD_3COCD_3}$, 213 K): δ 18.9, 20.3 (s, $\mathrm{PCH(}\mathit{C}\mathrm{H_3)_2}$), 26.8 (s, $^{i}\mathrm{Pr_2P}\mathit{C}\mathrm{H_2CH{=}CH_2}$), 117.2 (s, $^{i}\mathrm{Pr_2PCH_2CH{=}}\mathit{C}\mathrm{H_2}$), 134.6 (s, $^{i}\mathrm{Pr_2PCH_2}\mathit{C}\mathrm{H{=}CH_2}$).

$[\mathrm{Ni(\eta^3\text{-}CH_2C(R)CH_2)(\kappa^1}\mathit{P}\text{-}\mathrm{PPh_2CH_2CH{=}CH_2)}][\mathrm{BAr'_4}]$ (R = H 4a, Me 4b)

To a slurry of $[\mathrm{Ni(COD)_2}]$ (0.54 g, 2 mmol) in diethyl ether (20 mL) cooled in a liquid $\mathrm{N_2}$–ethanol bath, allyl bromide (for **4a**, 173 μL) or 2-methyl-1-bromopropene (for **4b**, 205 μL) was added. The mixture was warmed to room temperature and stirred for 1 h. During this time it changed from yellow to red. At this stage $\mathrm{NaBAr'_4}$ (1.76 g, 2 mmol) was added, and the mixture was stirred for 1 h. During this time the color changed from red to orange. Diphenylallylphosphine (0.44 mL, 2 mmol) was added. The mixture was stirred for 15 min, and then filtered through Celite. The solvent was removed *in vacuo*, and the resulting sticky solid was repeatedly triturated and washed with petroleum ether until a yellow-orange powder was obtained. Recrystallisation from dichloromethane–petroleum ether afforded in both cases yellow-orange crystals, which were filtered off, washed with petroleum ether and dried *in vacuo*.

Data for 4a. Yield: 2 g, 72%. Anal. Calcd for $\mathrm{C_{65}H_{47}BF_{24}NiP_2}$: C, 55.2; H, 3.35. Found: C, 55.0; H, 3.28%. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 298 K) δ 2.61 (m, 6 H, $\mathrm{Ph_2PC}\mathit{H}_2\mathrm{CH{=}CH_2}$ + $\mathrm{CH^{\mathit{syn}}}\mathit{H}^{\mathit{anti}}\mathrm{CHCH^{\mathit{syn}}}\mathit{H}^{\mathit{anti}}$), 3.89 (br, 2 H, $\mathrm{C}\mathit{H}^{\mathit{syn}}\mathrm{H^{\mathit{anti}}CHC}\mathit{H}^{\mathit{syn}}\mathrm{H^{\mathit{anti}}}$), 4.83, 5.03 (d, 2 H each, $\mathrm{Ph_2PCH_2CH{=}C}\mathit{H}_2$), 5.32 (m, 1 H, $\mathrm{CH_2C}\mathit{H}\mathrm{CH_2}$), 5.45 (m, 2 H, $\mathrm{Ph_2PCH_2C}\mathit{H}\mathrm{{=}CH_2}$), 7.10, 7.25, 7.37 (m, 20 H, $\mathrm{C_6}\mathit{H}_5$); ^{31}P{^{1}H} NMR (161.89 MHz, $\mathrm{CDCl_3}$, 298 K): δ 16.48 (s); ^{13}C{^{1}H} NMR (100.57 MHz, $\mathrm{CDCl_3}$, 298 K): δ 34.0 (d, $^{1}J_{\mathrm{CP}}$ = 23.5 Hz, $\mathrm{Ph_2P}\mathit{C}\mathrm{H_2CH{=}CH_2}$), 71.7 (br, $\mathit{C}\mathrm{H_2CH}\mathit{C}\mathrm{H_2}$), 116.3 (s, $\mathrm{CH_2}\mathit{C}\mathrm{HCH_2}$), 121.7 (br, $\mathrm{Ph_2PCH_2CH{=}}\mathit{C}\mathrm{H_2}$), 128.7 (s, $\mathrm{Ph_2PCH_2}\mathit{C}\mathrm{H{=}CH_2}$), 129.3, 131.8, 132.1 ($\mathit{C}_6\mathrm{H_5}$).

Data for 4b. Yield: 2.16 g, 77%. Anal. Calcd for $\mathrm{C_{66}H_{49}BF_{24}NiP_2}$: C, 55.5; H, 3.45. Found: C, 55.6; H, 3.62%. ^{1}H NMR (400 MHz, $\mathrm{CD_3COCD_3}$, 298 K): δ 1.94 (s, 3 H, $\mathrm{CH_2C(C}\mathit{H}_3\mathrm{)CH_2}$), 3.03 (br, 2 H, $\mathrm{CH^{\mathit{syn}}}\mathit{H}^{\mathit{anti}}\mathrm{C(CH_3)CH^{\mathit{syn}}}\mathit{H}^{\mathit{anti}}$), 3.11 (br, 4 H, $\mathrm{Ph_2PC}\mathit{H}_2\mathrm{CH{=}CH_2}$), 3.83 (br, 2 H, $\mathrm{C}\mathit{H}^{\mathit{syn}}\mathrm{H^{\mathit{anti}}}$-$\mathrm{C(CH_3)C}\mathit{H}^{\mathit{syn}}\mathrm{H^{\mathit{anti}}}$), 4.99, 5.07 (d, 2 H each, $\mathrm{Ph_2PCH_2CH{=}C}\mathit{H}_2$), 5.72 (br, 1 H, $\mathrm{Ph_2PCH_2C}\mathit{H}\mathrm{{=}CH_2}$), 7.44, 7.51 (m, 20 H, $\mathrm{C_6}\mathit{H}_5$); ^{31}P{^{1}H} NMR (161.89 MHz, $\mathrm{CD_3COCD_3}$, 298 K): δ 19.10 (s); ^{13}C{^{1}H} NMR (75.4 MHz, $\mathrm{CD_3COCD_3}$, 298 K): δ 22.9 (s, $\mathrm{CH_2C(}\mathit{C}\mathrm{H_3)CH_2}$), 34.0 (d, J_{CP} = 25.6 Hz, $\mathrm{Ph_2P}\mathit{C}\mathrm{H_2CH{=}CH_2}$), 71.6 (br, $\mathit{C}\mathrm{H_2C(CH_3)}\mathit{C}\mathrm{H_2}$), 119.8 (s, $\mathrm{CH_2}\mathit{C}\mathrm{(CH_3)CH_2}$), 120.9 (d, J_{CP} = 8.5 Hz, $\mathrm{Ph_2PCH_2CH{=}}\mathit{C}\mathrm{H_2}$), 130.1 (s, $\mathrm{Ph_2PCH_2}\mathit{C}\mathrm{H{=}CH_2}$), 129.6, 131.7, 133.5 (m, $\mathit{C}_6\mathrm{H_5}$).

$[\mathrm{Ni(\eta^3\text{-}CH_2C(R)CH_2)(\kappa^1}\mathit{P}\text{-}\mathrm{P^iPr_2CH_2CH{=}CH_2)_2}][\mathrm{BAr'_4}]$ (R = H 5a, R = Me 5b)

These compounds were prepared by a identical procedure to that for **4a–b**, using $\mathrm{P^iPr_2CH_2CH{=}CH_2}$ (0.30 mL, 2 mmol) instead of $\mathrm{PPh_2CH_2CH{=}CH_2}$.

Data for 5a. Yield: 1.83 g, 73%. Anal. Calcd for $\mathrm{C_{53}H_{55}BF_{24}NiP_2}$: C, 49.8; H, 4.33. Found: C, 49.9; H, 4.51%. ^{1}H NMR (400 MHz, $\mathrm{CD_2Cl_2}$, 298 K): δ 1.22 (m, 24 H, $\mathrm{PCH(C}\mathit{H}_3\mathrm{)_2}$), 2.25 (m, 4 H, $\mathrm{PC}\mathit{H}\mathrm{(CH_3)_2}$), 2.45 (d, J_{HH} = 13.2 Hz, 2 H, $\mathrm{CH^{\mathit{syn}}}\mathit{H}^{\mathit{anti}}\mathrm{CHCH^{\mathit{syn}}}\mathit{H}^{\mathit{anti}}$), 2.76 (m, 4 H, $^{i}\mathrm{Pr_2PC}\mathit{H}_2\mathrm{CH{=}CH_2}$), 4.27 (br, 2 H, $\mathrm{C}\mathit{H}^{\mathit{syn}}\mathrm{H^{\mathit{anti}}CHC}\mathit{H}^{\mathit{syn}}\mathrm{H^{\mathit{anti}}}$), 5.26, 5.28 (d, 2 H each, $^{i}\mathrm{Pr_2PCH_2CH{=}C}\mathit{H}_2$), 5.58 (br, 1 H, $\mathrm{CH_2C}\mathit{H}\mathrm{CH_2}$), 5.79 (br, 2 H, $^{i}\mathrm{Pr_2PCH_2C}\mathit{H} = \mathrm{CH_2}$). ^{31}P{^{1}H} NMR (161.89 MHz, $\mathrm{CD_3COCD_3}$, 298 K): δ 32.2 (s); ^{13}C{^{1}H} NMR (75.4 MHz, $\mathrm{CD_2Cl_2}$, 298 K): δ 18.8, 18.9, 19.9 (s, $\mathrm{PCH(}\mathit{C}\mathrm{H_3)_2}$), 26.8 (m, $\mathrm{P}\mathit{C}\mathrm{H(CH_3)_2}$), 28.2 (m, $^{i}\mathrm{Pr_2P}\mathit{C}\mathrm{H_2CH{=}CH_2}$), 66.0 (br, $\mathit{C}\mathrm{H_2CH}\mathit{C}\mathrm{H_2}$), 114.6 (s, $\mathrm{CH_2}\mathit{C}\mathrm{HCH_2}$), 121.2 (t, J_{CP} = 4.6 Hz, $^{i}\mathrm{Pr_2PCH_2CH{=}}\mathit{C}\mathrm{H_2}$), 128.7 (s, $^{i}\mathrm{Pr_2PCH_2}\mathit{C}\mathrm{H{=}CH_2}$).

Data for 5b. Yield: 1.95 g, 78%. Anal. Calcd for $\mathrm{C_{54}H_{57}BF_{24}NiP_2}$: C, 50.1; H, 4.44. Found: C, 50.4; H, 4.61%. ^{1}H NMR (400 MHz, $\mathrm{CD_3COCD_3}$, 298 K): δ 1.06–1.41 (m, 24 H, $\mathrm{PCH(C}\mathit{H}_3\mathrm{)_2}$), 2.01 (s, 3 H, $\mathrm{CH_2C(C}\mathit{H}_3\mathrm{)CH_2}$), 2.47 (m, 4 H, $\mathrm{PC}\mathit{H}\mathrm{(CH_3)_2}$), 2.78 (br, 2 H, $\mathrm{CH^{\mathit{syn}}}\mathit{H}^{\mathit{anti}}\mathrm{C(CH_3)CH^{\mathit{syn}}}\mathit{H}^{\mathit{anti}}$), 2.99 (m, 4 H, $^{i}\mathrm{Pr_2PC}\mathit{H}_2\mathrm{CH{=}CH_2}$), 4.25 (d, J_{HH} = 4.4 Hz, 2 H, $\mathrm{C}\mathit{H}^{\mathit{syn}}\mathrm{H^{\mathit{anti}}C(CH_3)C}\mathit{H}^{\mathit{syn}}\mathrm{H^{\mathit{anti}}}$), 5.23, 5.32 (d, 2 H each, $^{i}\mathrm{Pr_2PCH_2CH{=}C}\mathit{H}_2$), 6.01 (m, 2 H, $^{i}\mathrm{Pr_2PCH_2C}\mathit{H}\mathrm{{=}CH_2}$); ^{31}P{^{1}H} NMR (161.89 MHz, $\mathrm{CD_3COCD_3}$, 298 K): δ 33.3 (s); ^{13}C{^{1}H} NMR (75.4 MHz, $\mathrm{CD_2Cl_2}$, 298 K): δ 19.0, 19.2 (s, $\mathrm{PCH(}\mathit{C}\mathrm{H_3)_2}$), 20.2 (d, J_{CP} = 6.1 Hz, $\mathrm{PCH(CH_3)_2}$), 22.7 (s, $\mathrm{CH_2C(}\mathit{C}\mathrm{H_3)CH_2}$), 26.7 (m, $\mathrm{P}\mathit{C}\mathrm{H(CH_3)_2}$), 28.6 (m, $^{i}\mathrm{Pr_2P}\mathit{C}\mathrm{H_2CH{=}CH_2}$), 66.2 (m, $\mathit{C}\mathrm{H_2C(CH_3)}\mathit{C}\mathrm{H_2}$), 118.0 (s, overlapping with one $\mathrm{BAr'_4}$ resonance, $\mathrm{CH_2}\mathit{C}\mathrm{(CH_3)CH_2}$), 121.1 (t, J_{CP} = 4.6 Hz, $^{i}\mathrm{Pr_2PCH_2CH{=}}\mathit{C}\mathrm{H_2}$), 130.3 (t, J_{CP} = 3.3 Hz, $^{i}\mathrm{Pr_2PCH_2}\mathit{C}\mathrm{H{=}CH_2}$).

X-Ray structure determinations

Crystal data and experimental details are given in Table 3. X-Ray diffraction data were collected on a Bruker SMART APEX 3-circle diffractometer (graphite-monochromated MoK_{α} radiation, λ = 0.71073 Å) with CCD area detector at the Servicio Central

Table 3 Summary of crystallographic data for **1**, **2**, **3b** and **5b**

Compound	**1**	**2**	**3b**	**5b**
Formula	$C_{18}H_{20}BrNiP$	$C_{12}H_{24}BrNiP$	$C_{18}H_{38}Br_2NiP_2$	$C_{54}H_{57}P_2NiBF_{24}$
FW	405.93	337.90	534.95	1293.46
T/K	100	100	100	100
Crystal size/mm	0.07 × 0.16 × 0.29	0.17 × 0.35 × 0.49	0.30 × 0.36 × 0.40	0.18 × 0.24 × 0.37
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$Pbca$ (no. 61)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
a/Å	11.461(2)	12.436(3)	8.2979(17)	12.799(3)
b/Å	16.298(3)	7.4524(16)	15.238(3)	11.980(2)
c/Å	18.029(4)	15.775(4)	9.3390(19)	37.938(8)
β/°		96.071(4)	104.40(3)	99.13(3)
Volume/Å^3	3367.7(11)	1453.8(6)	1143.8(4)	5743(2)
Z	8	4	2	4
ρ_{calc}/g cm^{-3}	1.601	1.544	1.553	1.496
μ(MoKα)/cm^{-1}	36.1	41.6	44.8	5.08
F(000)	1648	696	548	2640
Max. and min. transmission factors	1.000 – 0.754	1.000 – 0.667	1.000 – 0.696	1.000 – 0.851
Theta range for data collection	$2.3 < \theta < 25.2$	$2.6 < \theta < 25.0$	$2.6 < \theta < 25.0$	$1.6 < \theta < 25.0$
Reflections collected	21191	5722	7892	35584
Unique reflections	2992 ($R_{int} = 0.055$)	2508 ($R_{int} = 0.059$)	2015 ($R_{int} = 0.028$)	10098 ($R_{int} = 0.048$)
No. of observed reflections ($I > 2\sigma I$)	2580	2143	1979	9238
No. of parameters	250	140	110	768
Final $R1$, $wR2$ values ($I > 2\sigma I$)	0.0341, 0.0772	0.0345, 0.0783	0.0265, 0.0588	0.0770, 0.1540
Final $R1$, $wR2$ values (all data)	0.0468, 0.0773	0.0403, 0.0804	0.0272, 0.0592	0.0860, 0.1594
Residual electron density peaks/e Å^{-3}	+0.90, −0.35	+0.86, −0.54	+0.44, −0.37	+0.81, −0.46

de Ciencia y Tecnología de la Universidad de Cádiz. Hemispheres of the reciprocal space were measured by omega scan frames with $\delta(\omega)$ 0.30°. Corrections for absorption and crystal decay (insignificant) were applied by semi-empirical methods from equivalents using the program SADABS.[33] 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.[34] The program ORTEP-3[35] was used for plotting.

Oligomerization reactions

General procedure. A Schlenk tube was loaded with 10 mmol of either styrene or 4-methylstyrene, 1,2-dichloroethane (1 mL) and the corresponding freshly-prepared catalyst (0.05 mol) under dinitrogen. In most cases, the system was warmed to 40 °C using a thermostatic bath. In other instances the reactions were performed at 25 °C. After the corresponding period of time, the deep red reaction mixture was quenched by addition of methanol. The volatiles were pumped off, and the residue treated with methanol to yield a white precipitate, which was filtered off and dried in vacuum. The oligostyrenes were dissolved in dichloromethane (10 mL), and filtered through a silica gel plug. The silica gel was washed with several small portions of dichloromethane in order to remove all traces of oligomer. The solvent was removed from the combined filtrate. The residue was treated with methanol until a powder was obtained. The resulting precipitate of oligostyrene or oligo(4-methylstyrene) was filtered off, washed with petroleum ether and dried in vacuum until constant weight.

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. The amounts of oligomer obtained in the blank reaction were negligible in all cases.

Hydrosilylation reactions

General procedure. A Schlenk tube was loaded with 2 mmol $PhSiH_3$, 1,2-dichloroethane (0.25 mL) and the corresponding freshly-prepared catalyst (0.01 mol) under dinitrogen. Then, 1 mmol of either styrene or 4-methylstyrene was added. The system was warmed up to 40 °C using a thermostatic bath. The mixture was stirred for 5 h at this temperature. After this period of time, a dark red solution was obtained. The volatiles were pumped off. The resulting oily residue was dissolved in dichloromethane, and passed through a silica column. Removal of the solvent afforded the corresponding hydrosilylation products in the form of yellowish oils. Their NMR properties were compared with data in the literature.[12,36]

NMR data for $C_6H_5CH(SiH_2Ph)CH_3$:^1H (400 MHz, $CDCl_3$, 298 K): δ 1.36 (d, $^3J_{HH} = 7.6$ Hz, 3 H, $CH(SiH_2Ph)CH_3$), 2.53 (m, 1 H, $CH(SiH_2Ph)CH_3$), 4.24 (s br, 2 H, $CH(SiH_2Ph)CH_3$), 7.00–4.50 (m, 10 H, C_6H_5). $^{13}C\{^1H\}$ (100.57 MHz, $CDCl_3$, 298 K): δ 16.6 (s, $CH(SiH_2Ph)CH_3$), 25.6 (s, $CH(SiH_2Ph)CH_3$), 122.3, 127.4, 128.1, 128.6, 130.0, 133.4, 135.9, 144.3 (s, C_6H_5).

NMR data for $CH_3C_6H_4CH(SiH_2Ph)CH_3$: ^1H (400 MHz, $CDCl_3$, 298 K): δ 1.47 (d, $^3J_{HH} = 6.8$ Hz, 3 H, $CH(SiH_2Ph)CH_3$), 2.33 (s, 3 H, $CH_3C_6H_4$), 2.62 (m, 1 H, $CH(SiH_2Ph)CH_3$), 4.35 (d, $^3J_{HH} = 2.8$ Hz, 2 H, $CH(SiH_2Ph)CH_3$), 7.00–7.50 (m, 9 H, C_6H_4, C_6H_5). $^{13}C\{^1H\}$ (100.57 MHz, $CDCl_3$, 298 K): δ 16.6 (s, $CH(SiH_2Ph)CH_3$), 20.9 (s, $CH_3C_6H_4$), 24.8 (s, $CH(SiH_2Ph)CH_3$), 127.0, 127.8, 129.1, 129.7, 133.2, 135.6, 141.5 (s, C_6H_4, C_6H_5).

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