Stable Nickel Catalysts for Fast Norbornene Polymerization: Tuning Reactivity

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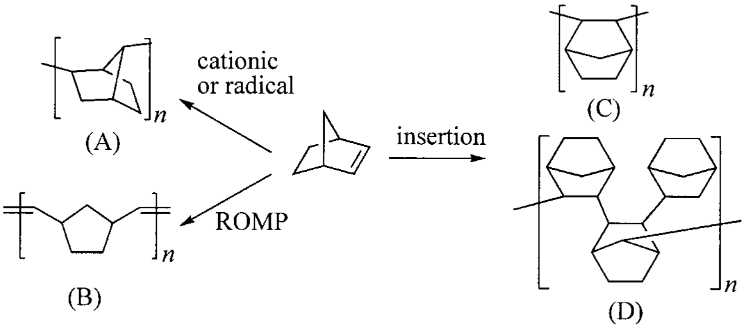
The air-stable complexes *trans*-[Ni($C_6Cl_2F_3$)$_2$$L_2$] (L = $SbPh_3$, **1**; $AsPh_3$, **2**; $AsCyPh_2$, **3**; $AsMePh_2$, **4**; PPh_3, **5**) have been synthesized by arylation of [$NiBr_2$(dme)] (dme = 1,2-dimethoxyethane) in the presence of the corresponding ligand L (for compounds **1**–**4**) or by ligand substitution starting from **1** (for compound **5**). The structures of **1**, **2**, and **5** have been determined by X-ray diffraction and show an almost perfect square-planar geometry in all cases. Their catalytic activity in insertion polymerization of norbornene have been tested showing a strong dependence of the yield and molecular mass of the polymer on the ligand used and the solvent. High yield and high molecular mass values are obtained using complexes with ligands easy to displace from Ni^{II} ($SbPh_3$ is the best) and noncoordinating solvents. Complexes **1**–**3** are suggested as convenient bench-catalysts to have available in the lab.

Introduction

The increasing interest in the polymerization of cyclic olefins is due to the attractive properties of these polymers, which show high glass transition temperatures, high optical transparency, low dielectric constant and low birefringence. Starting from norbornene (bicyclo[2.2.1]hept-2-ene) and norbornene derivatives, different classes of polymers can be obtained by selecting polymerization conditions that drive the reaction by cationic or radical pathways, by ring-opening metathesis, or by insertion routes (Scheme 1).[1]

Cationic polymerization of norbornene results in the formation of low molecular mass polymers with rearranged norbornanediyl units in the backbone (A). Metal catalyzed ring-opening metathesis polymerization (ROMP) of norbornene derivatives yields polymers containing unsaturations in the backbone (B). Metal-catalyzed insertion polymerization of norbornene, either with early transition metallocene complexes or with late transition organometallics can lead to two different structures, one strictly linear containing norbornanediyl units (C), and another in which norbornanediyl and rearranged norbornanediyl with appended norbornanediyl units alternate (D).[1,2]

A number of nickel complexes are very efficient catalysts for the vinyl polymerization of norbornene, for the copolymerization of functionalized norbornenes, and also for the copolymerization of norbornene with ethene.[1,3–9] Usually the polymerization requires a nickel(II) catalyst and an organometallic co-catalyst [typically methylaluminoxane or $B(C_6F_5)_3$],[1,3,7,8,10] but a few nickel organometallics (cationic allyl complexes such as [Ni(η^3-crotyl)(1,4-COD)]PF_6, some phenyl derivatives, and [Ni(C_6F_5)$_2$(η^6-toluene)]), are very efficient without co-catalyst.[1,8,9] Noteworthy, although the use of monodentate ligands, particularly phos-



Scheme 1.

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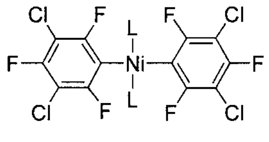
phanes, has been reported in the patent literature,[11] most of the catalysts used are stabilized by multidentate chelating ligands.

In this paper we report the synthesis of complexes *trans*-[Ni($C_6Cl_2F_3$)$_2$L$_2$] (L = SbPh$_3$, AsPh$_3$, AsCyPh$_2$, AsMePh$_2$, or PPh$_3$) and their catalytic activity in insertion polymerization of norbornene. In these compounds the monodentate ligands are able to stabilize the complexes allowing their manipulation as solids in the air, but are labile and weak enough to give highly active catalytic systems in solution.

Results and Discussion

Synthesis and Behavior in Solution

The reaction of [NiBr$_2$(dme)] (dme = 1,2-dimethoxyethane) with Li($C_6Cl_2F_3$) and L (molar ratio 1:1:2.2) in diethyl ether affords the yellow air-stable complexes *trans*-[Ni($C_6Cl_2F_3$)$_2$L$_2$] (L = SbPh$_3$, **1**; AsPh$_3$, **2**; AsCyPh$_2$, **3**; AsMePh$_2$, **4**) (Scheme 2). With PPh$_3$ this procedure affords *trans*-[Ni($C_6Cl_2F_3$)$_2$(PPh$_3$)$_2$] (**5**) along with a number of byproducts, not further identified, which lowered the yield. Thus, complex **5** is better prepared by the reaction of **1** with PPh$_3$ in chloroform (molar ratio 1:2), followed by solvent evaporation, and removal of the displaced ligand SbPh$_3$ with diethyl ether. In fact *trans*-[Ni($C_6Cl_2F_3$)$_2$(SbPh$_3$)$_2$] is a fairly general precursor for other [Ni($C_6Cl_2F_3$)$_2$L$_2$] complexes.



L	Complex
SbPh$_3$	1
AsPh$_3$	2
AsCyPh$_2$	3
AsMePh$_2$	4
PPh$_3$	5

Scheme 2.

All the complexes reported in this paper are *trans* isomers. The structures of **1**, **2** and **5** have been determined by X-ray diffraction. They are very similar and only the structure of **5** is shown in Figure 1. Crystallographic data are given in Table 3 (see Experimental Section). Selected interatomic distances and angles are shown in Table 1. The complexes crystallized in the P-1 group with one molecule in the asymmetric unit for compound **5**, and just half a molecule in the asymmetric unit for compounds **1** and **2**. The three compounds are almost perfectly square planar, with angles between adjacent donor atoms very close to 90° and the two haloaryl ligands mutually *trans*. The Ni–C bond lengths are very similar to those found in the two *trans*-bis(pentafluorophenyl)nickel complexes reported to date (1.939 Å in both [Ni(C_6F_5)$_2$(PMePh$_2$)$_2$] and [Ni(C_6F_5)$_2$(CN*t*Bu)$_2$]).[18,20] The Ni–P distances [2.2467(9) and 2.2544(8) Å] are in the upper limit of the range found in the Cambridge Structural Database for *trans*-bis(triphenylphosphane)nickel complexes (2.220–2.253 Å).[12] The Ni–As and Ni–Sb distances cannot be compared to reference values in the literature because the Ni complexes with AsPh$_3$ or SbPh$_3$ reported (one with each ligand) are not structurally similar.[13,14] The haloaryl rings are almost perpendicular to the coordination plane in the three molecules, with tilting

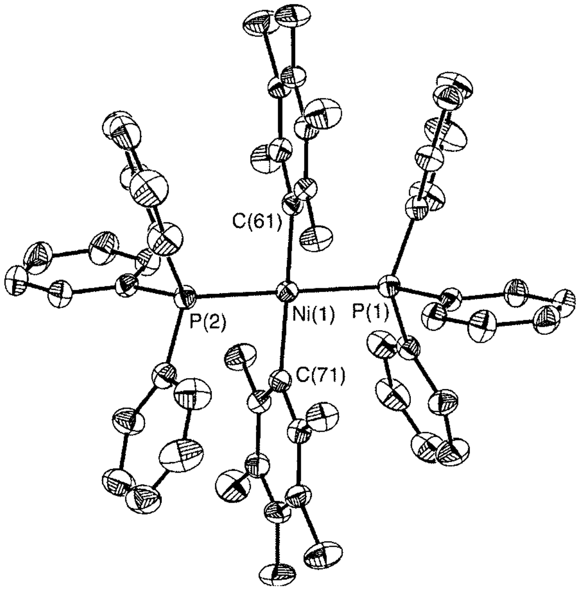


Figure 1. ORTEP diagram of the molecular structure of complex *trans*-[Ni($C_6Cl_2F_3$)$_2$(PPh$_3$)$_2$] (**5**). All hydrogen atoms have been omitted for clarity. Atoms are shown as displacement ellipsoids enclosing 30% probability density.

Table 1. Selected bond lengths [Å] and angles [°] for **1**, **2** and **5**.

1		**2**		**5**	
Ni(1)–C(31)	1.926(5)	Ni(1)–C(1)	1.933(3)	Ni(1)–C(61)	1.938(2)
				Ni(1)–C(71)	1.951(2)
Ni(1)–Sb(1)	2.4480(6)	Ni(1)–As(1)	2.3094(7)	Ni(1)–P(2)	2.2467(9)
				Ni(1)–P(1)	2.2544(8)
C(31)–Ni(1)–Sb(1)	88.36(13)	C(1)–Ni(1)–As(1)	90.11(9)	C(61)–Ni(1)–P(1)	91.03(6)
				C(71)–Ni(1)–P(1)	90.45(7)
				C(61)–Ni(1)–P(2)	89.33(7)
				C(71)–Ni(1)–P(2)	89.21(7)

angles ranging from 83.2(2) to 89.3(2)°. The phosphane ligands are staggered and one phenyl ring on each phosphane is parallel to one haloaryl ring.

The stereochemical preferences of complexes [Ni(aryl)$_2$-L$_2$] are strongly dependent on the nature of L. Electronically, the *cis* isomers, avoiding *trans* arrangements of substituents with high *trans*-influence, should be preferred, and this is often determinant for Pd and Pt complexes.[15] However, steric factors seem important in the smaller Ni. In fact, structures containing some of the ligands used here have *cis* feature L–Ni–L angles noticeably larger than 90°,[16] indicating steric repulsion between the ligands. This suggests that the preference for the *trans* isomer found here must be largely associated to a minimization of steric repulsions. Related complexes with arylphosphanes also show a preference for *trans* stereochemistry, as found for [Ni(C_6F_5)$_2$-(PMePh$_2$)$_2$],[17,18] and [Ni(4-C_6BrF_4)$_2$(PMePh$_2$)$_2$] in solution ($CDCl_3$ or CD_2Cl_2) and in the solid state.[19] [Ni-(4-C_6BrF_4)$_2$(PMePh$_2$)$_2$] is formed as a mixture of the *cis* and *trans* isomers which slowly converts completely into the most stable *trans* isomer. On the other hand, for complexes involving less sterically demanding ligands, such as [PPh$_3$Me][Ni(C_6F_5)$_2$Br(CO)], [Ni(C_6F_5)$_2$(CO)$_2$], and [Ni(C_6F_5)$_2$(THF)$_2$], only the *cis* isomer is obtained.[20] The NMR spectra of **1**–**5** in $CDCl_3$ show the presence of just one compound in solution. The spectra at room temperature are coincident with those recorded at 213 K on samples dissolved at low temperature, supporting the suggestion that the signals arise from the *trans* isomer present in the solid state.

Complexes **1**–**5** are stable in the solid state and can be stored for long periods, but they decompose slowly in solution in $CDCl_3$ or [D$_6$]acetone at 298 K (in times much larger than the polymerization reactions). The decomposition is faster for **1** than for **2**–**4**, and is very slow for **5**. The major F-containing decomposition product is the coupling compound $C_6Cl_2F_3$–$C_6Cl_2F_3$ (**6**), along with small amounts of $C_6Cl_2F_3H$ (**7**) and other very minor noncharacterized products. A similar decomposition pattern has been reported for related pentafluorophenyl derivatives.[21]

Catalyzed Polymerization of Norbornene

The catalytic reactions were carried out under nitrogen at room temperature. In CH_2Cl_2 the polymerization started in seconds without cocatalysts, producing a white precipitate of polymer. After 30 min the reactions were quenched pouring the reacting mixtures over MeOH. Data concerning the polymers obtained are reported in Table 2. No attempts were made to optimize the yield or M_w of the polymer. Polymerization runs using **1** as a catalyst under air gave the same results.

Table 2. Norbornene polymerization catalyzed by **1**–**5** (reaction conditions unless otherwise stated: 9.2 mmol of norbornene and 4.6 µmol of catalyst in 3 mL of CH_2Cl_2; reaction time: 30 min).

Entry	Catalyst	Yield [%]	$M_w/10^5$	M_w/M_n
1	**1**	90	12.59	2.4
2	**2**	75	6.06	4.6
3	**3**	72	6.05	4.9
4	**4**	3	2.11	2.1
5	**5**	traces	0.1	
6	**1**[a]	–	–	
7	**1**[b]	17	0.99	
8	**1**[c]	0	–	
9	**1**[d]	18	0.1	

[a] Solvent: acetone. [b] Solvent: acetone; reaction time: 24 h. [c] 5-Norbornene-2-carboxaldehyde instead of norbornene. [d] A 3:1 mixture of norbornene/5-norbornene-2-carboxaldehyde instead of norbornene.

The ^{13}C NMR spectra of the polynorbornene obtained in these experiments were identical to that reported by Barnes et al. using [Ni(dpm)$_2$]/AlEt$_3$/B(C_6F_5)$_3$ (dpm = 2,2,6,6-tetramethyl-3,5-heptanedionate) and (pentafluorophenyl)nickel complexes as catalysts. The absence of resonances in the 20–24 ppm region has been taken as indicative of *exo*-enchained norbornene-based polymers, generated by an insertion mechanism.[9] The ^{19}F NMR spectra in $CDCl_3$ showed mainly three 1:1:1 signals (–112.0, –115.3, –115.5 ppm), together with signals due to the coupling product **6** and smaller signals due to the hydrolysis product **7**, which remain adsorbed to the polymer, and to unidentified products (–105.1, –106.0, –111.9 ppm). Repeated washing with toluene removes the signals of **6** and **7**, but not the other minor signals. The chemical shifts of the 1:1:1 signals are typical of a $C_6Cl_2F_3$ group bonded to a carbon atom and can be assigned to the perhaloaryl group bonded to the polymer. The chemical shift of the $C_6Cl_2F_3$ fluorine nuclei are very sensitive to the group substituents.[22] A similar effect has been observed in the ^{19}F NMR of the pentafluorophenyl group bonded to metal or to carbon atoms.[23] The presence of three signals indicates that the two F_{ortho} atoms are nonequivalent because the rotation of the $C_6Cl_2F_3$ group around the phenyl *ipso*-carbon–norbornene carbon single bond is hindered according to the results reported by Barnes et al.[9] In the case of the $C_6Cl_2F_3$ group the chemical shifts for F_{ortho} and F_{para} do not permit us to assign them unambiguously and an attempt to correlate (hence recognize) the F_{ortho} atoms by spin saturation transfer at 323 K was unsuccessful, revealing that there is no detectable exchange of the two F_{ortho} signals at this temperature. In our compounds we do not see a splitting of any of the F_{ortho} signals, a phenomenon which was reported in the case of C_6F_5 by Barnes et al.[9] This may well be because of the fact that all chemical shift differences are smaller in our system.

A clear dependence of the yield of the polymer on the ligand in the catalysts is observed: the yield in polymer is high for complexes with SbPh$_3$, AsPh$_3$, and AsCyPh$_2$, but drops dramatically for AsMePh$_2$ and PPh$_3$. The very high yield and M_W found with complex **1** (SbPh$_3$ as the ligand) are comparable to that found previously for the three component catalyst [Ni(dpm)$_2$]/AlEt$_3$/B(C_6F_5)$_3$.[9] The higher stability in the solid state of **1** compared to [Ni(C_6F_5)$_2$-(η^6-toluene)], which is air and moisture sensitive, is advantageous. The influence of the ligand on the reaction can be understood assuming that equilibria 1 and 2 govern the concentration of the active species in solution. Ligands that are better donors and have less steric requirement shift these equilibria to the left, making the complexes inactive.

$$[\mathrm{Ni}(\mathrm{C_6Cl_2F_3})_2\mathrm{L_2}] + \mathrm{NB} \rightleftharpoons [\mathrm{Ni}(\mathrm{C_6Cl_2F_3})_2(\mathrm{NB})\mathrm{L}] + \mathrm{L} \qquad (1)$$

$$[\mathrm{Ni}(\mathrm{C_6Cl_2F_3})(\mathrm{P})\mathrm{L_2}] + \mathrm{NB} \rightleftharpoons [\mathrm{Ni}(\mathrm{C_6Cl_2F_3})(\mathrm{P})(\mathrm{NB})\mathrm{L}] + \mathrm{L} \qquad (2)$$

(P = polymer chain)

The effect of the bulkiness of the ligand on the properties of the polymer has been studied by Lipian et al. for cationic allylpalladium(II) complexes with selected phosphanes as the catalyst.[24] For these catalysts the bulkier the phosphane the lower the molecular mass of the polymer, while high conversion is always observed. The opposite trend is observed here comparing complexes **3** (containing $AsCyPh_2$) and **4** (containing $AsMePh_2$). This suggests a different ligand role for both types of catalyst. While no ligand dissociation is required in the palladium complexes employed by Lipian et al. (the bulkier phosphane is simply hindering more norbornene coordination or insertion), in complexes **1**–**5** the displacement of one ligand by the entering norbornene is required to carry out the polymerization process. For similar electronic characteristics displacement of a bulkier ligand $AsCyPh_2$ in equilibria 1 and 2 is favored compared to the displacement of $AsMePh_2$ and this turns out to be the dominant fact. Similarly, the molecular mass of the polymer increases with the same ligands that increase the overall yield of the reaction.

The reaction between **1** and norbornene in CD_2Cl_2 was monitored by ^{19}F NMR (norbornene:**1** = 200:1). No signals of Ni complexes containing $C_6Cl_2F_3$ other than **1** were detected throughout the experiment. This suggests that **1** is a precatalyst, from which the catalyst is formed in a small nonobservable proportion. At low temperature (–60 °C) no reaction takes place at an observable rate. At –10 °C the white polymer starts to precipitate from the solution and very broad $C_6Cl_2F_3$ signals appear corresponding to the ones mentioned earlier. At 0 °C the solution becomes very viscous in a few minutes, giving rise to a broadening of all the signals in the spectrum.

The polymerization of O-functionalyzed norbornenes with Ni catalysts has been reported in the literature, although using a higher catalyst/monomer ratio.[8] Even in these conditions the yield and M_w values are low, and the authors attribute the low reactivity of O-functionalyzed norbornenes in part to the coordinating ability of the oxygen. Examples of the poisoning effect of palladium catalysts due to the coordination of the O-donor groups of functionalyzed norbornenes have been recently reported.[27]

The polymerization of 5-norbornene-2-carboxaldehyde was attempted with **1** as the catalyst, but no reaction was observed after 30 min, in agreement with the observations just discussed. Moreover, 5-norbornene-2-carboxaldehyde inhibits the polymerization in mixtures with norbornene and only a small amount of oligomers is obtained (Table 2, entries 8 and 9). The reaction of 5-norbornene-2-carboxaldehyde with **1** was monitored by ^{19}F NMR spectroscopy. In a 1:1 ratio no reaction takes place. If the ratio of the monomer is increased up to 100:1 no new signals of Ni-bonded $C_6Cl_2F_3$ groups appear, but weak peaks of organic $C_6Cl_2F_3$ arise. Apparently, the aldehyde group is not able to stabilize any Ni intermediate formed after norbornene insertion into the C–Ni bond, nor is the carboxylic group able to displace the $SbPh_3$ ligands coordinated to nickel, at least in a detectable extension. At room temperature the oligomerization of the monomer takes place slowly in the NMR tube, giving very broad signals due to $C_6Cl_2F_3$ bonded to carbon.

Further support of the detrimental effect of the presence of O-donors in norbornene polymerizations, whether intramolecular (O-functionalyzed norbornenes) or external (O-containing solvents) is provided by the results found for polymerization of norbornene in acetone: No polymerization of norbornene was observed after 30 min at 25 °C. Only after 24 h could a small amount of polynorbornene be detected (Table 2, entries 6 and 7). In other words, the catalytic activity is severely reduced, although not completely suppressed, in acetone. The small amount of white polymer precipitated from the acetone solution after 24 h at 25 °C was dissolved in $CDCl_3$ and showed in the ^{19}F NMR spectrum the same signals of $C_6Cl_2F_3$ discussed for the polymers obtained in CH_2Cl_2. However, the M_w of this polymer (Table 2 entry 7) is much lower than the M_w of the polymers obtained in CH_2Cl_2.

^{19}F NMR spectra of solutions of **1** in acetone revealed a complicated equilibrium between four different complexes, arising from partial substitution of $SbPh_3$ by acetone or water, with only 2% remaining as complex **1**.[25] The interpretation of this is that the most active catalyst in solution is complex **1**, which has a lower concentration in an acetone solution than in noncoordinating solvents, hence showing a reduced activity. Moreover, the substitution equilibria 1 and 2, which give rise to the species on which insertion takes place, are now further disfavored by the presence of considerable concentrations of free ligand, displaced from **1** by solvent or water. The rate corresponding to direct catalysis by aquo or acetone complexes is likely to be negligible, given the strong ligation of these O-donor ligands to Ni. This interpretation fits well with the general hypothesis that oxygen donors block the Ni catalyst.[8,24,26,27]

Conclusions

The results show that some *trans* diaryl nickel complexes containing monodentate ligands, stable and easy to store and handle, are very efficient catalysts for norbornene polymerization. There is a strong dependence of the yield and molecular mass of the polymer on the ligand used: yields and M_w's are higher for complexes with $SbPh_3$ (the best), $AsPh_3$, and $AsCyPh_2$, which are ligands easy to displace from Ni^{II}, but ligands more strongly bonded to the metal, such $AsMePh_2$ or PPh_3 (the worst) give less efficient catalysts. The inability of the complexes to polymerize substituted norbornene containing O-donor groups is related to the fact that the norbornene olefin bond is not able to displace the O-coordinating ligands even under high concentration conditions. Finally, the use of coordinating O-donor solvents or water is extremely detrimental.

In view of their catalytic activity in norbornene polymerization, their thermal and air stability, and their easy preparation, compounds **1**–**3** are choice reagents to have available.

Experimental Section

General Methods: All reactions were carried out under N_2 except when stated otherwise. Solvents were distilled using standard methods. The starting compound [$NiBr_2$dme],[28] the ligand $AsMePh_2$,[29] and solutions of $LiC_6Cl_2F_3$ were prepared by published methods.[30] Combustion CHN analyses were made with a Perkin–Elmer 2400 CHN microanalyzer. IR spectra were recorded with a Perkin–Elmer FT 1720 X spectrophotometer. Molecular masss of polymer were determined with a Waters SEC system equipped with a refractive index detector, using a three-column bed operating at 40 °C in $CHCl_3$ and calibrated to polystyrene narrow distribution standards. GS-MS data were obtained with a Hewlett–Packard 6890N gas chromatograph mass spectrometer (5973).

NMR spectra: ^{1}H NMR (300.16 MHz), ^{19}F NMR (282.4 MHz), and ^{31}P NMR (121.4 MHz) spectra were recorded with Bruker ARX 300 and AC 300 instruments equipped with a VT-100 variable-temperature probe. Chemical shifts are reported in ppm from $SiMe_4$ (^{1}H), CCl_3F (^{19}F), or H_3PO_4 (85%) (^{31}P) with positive shifts downfield, at ambient probe temperature unless otherwise stated. *J* values are given in Hz. ^{13}C NMR were registered as ^{1}H-^{13}C correlation experiments, which were made with a HMQC sequence with BIRD selection and GARP decoupling during acquisition. Chemical shifts of quaternary carbons are not listed in the experimental data.

Synthesis of $AsBrPh_2$: A solution of $LiAsPh_2$ was prepared from Li (0.557 g, 80.25 mmol), and $AsPh_3$ (9.187 g, 30.00 mmol) in THF (60 mL) as reported in the literature.[31] The solution was filtered with a cannula, cooled to –80 °C and Br_2 (3.1 mL, 60.50 mmol) was added very slowly. The solution was left to warm up to room temperature whilst stirring, whereupon it changed from deep red to orange. Then, solvent was removed and the resulting black residue was treated with CH_2Cl_2 (20 mL) and a saturated solution of NH_4Br in water (40 mL). The organic layer was decanted and the aqueous layer was subsequently extracted with CH_2Cl_2 (2 × 10 mL). Organic layers were dried with anhydrous $MgSO_4$, filtered and the solvent was vacuum evaporated. $AsBrPh_2$ (yellow oil) was obtained from the resulting residue after distillation at 170 °C and 5 mbar. Yield: 4.438 g (48%). $C_{12}H_{10}AsBr$ (309.04): calcd. C 46.64, H 3.26; found C 46.32, H 3.07. ^{1}H NMR ($CDCl_3$, 293 K): δ = 7.67–7.63 (m, 4 H), 7.44–7.40 (m, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 293 K): δ = 134.5, 133.3, 130.8, 129.6 ppm.

Synthesis of $AsCyPh_2$: A solution of MgCyCl in diethyl ether (35 mL) was prepared refluxing Mg (0.509 g, 20.94 mmol) and CyCl (2.0 mL, 16.86 mmol) for 6 h. The mixture was then cooled in an ice bath and a solution of $AsBrPh_2$ (2.321 g, 7.51 mmol) in THF (20 mL) was slowly added dropwise over 15 min. The stirring was maintained for another 30 min. The system was opened to air and acidified water (30 mL) was added. The organic layer was decanted and the aqueous layer was extracted with diethyl ether (3 × 10 mL). The organic solution was dried with anhydrous $MgSO_4$ and filtered and the solvent was vacuum evaporated. $AsCyPh_2$ was obtained as a yellow oil. After one day at –20 °C it became a white crystalline solid. Yield: 1.898 g (81%). $C_{18}H_{21}As$ (312.29): calcd. C 69.23, H 6.78; found C 68.79, H 6.57. ^{1}H NMR ($CDCl_3$, 293 K): δ = 7.50 (m, 4 H, Ph), 7.38–7.31 (m, 6 H, Ph), 2.33 (m, 1 H, C*H*, Cy), 1.77 (m, 5 H, Cy), 1.32 (m, 5 H, Cy) ppm. ^{13}C NMR ($CDCl_3$, 293 K): δ = 139.4, 133.6, 128.4, 128.2 ppm.

Synthesis of *trans*-[$Ni(C_6Cl_2F_3)_2(SbPh_3)_2$] (1): *n*-Butyllithium (8.5 mL of 1.2 M solution in hexane, 10.20 mmol) was added dropwise to a solution of 1,3,5-$C_6Cl_3F_3$ (2.402 g, 10.20 mmol) in dry Et_2O (50 mL), at –78 °C. After the reaction mixture was stirred at this temperature for 1 h, $SbPh_3$ (4.322 g, 12.24 mmol) and [$NiBr_2$(dme)] (1.574 g, 5.10 mmol) were added, and the suspension obtained was stirred overnight and allowed to warm to room temperature. Wet Et_2O (20 mL) was added and the suspension evaporated to dryness. The residue was extracted with $CHCl_3$ (60 mL) and the filtrate was evaporated to 5 mL, treated with ethanol (20 mL), and concentrated to 20 mL. The resulting suspension was filtered and the yellow solid washed with ethanol and air dried. Yield: 2.94 g (50%). $C_{48}H_{30}Cl_4F_6NiSb_2$ (1164.78): calcd. C 49.50, H 2.60; found C 49.14, H 2.76. ^{1}H NMR ($CDCl_3$, 293 K): δ = 7.34–7.25 (m, 30 H, Ph) ppm. ^{19}F NMR ($CDCl_3$, 293 K): δ = –87.47 (s, 4 F, F_{ortho}), –119.46 (s, 2 F, F_{para}) ppm.

Synthesis of *trans*-[$Ni(C_6Cl_2F_3)_2(AsPh_3)_2$] (2): To a solution of $LiC_6Cl_2F_3$ prepared from $C_6Cl_3F_3$ (1.181 g, 5.02 mmol) and BuLi (5.02 mmol) at –78 °C, were added $AsPh_3$ (1.837 g, 6.00 mmol) and [$NiBr_2$(dme)] (0.772 g, 2.50 mmol), the brown suspension obtained was stirred for 12 h and allowed to warm to room temperature. After that time the flask was opened to the air and wet diethyl ether (15 mL) was added in order to hydrolyze the organolithium excess. The solution was filtered and the resulting red solution was concentrated until dryness. The residue was treated with $CHCl_3$ (30 mL), the obtained suspension was filtered, and the resulting orange solution was concentrated until dryness. The crude product was recrystallized from $CHCl_3$/EtOH. Yield: 1.39 g (52%). $C_{48}H_{30}As_2Cl_4F_6Ni$ (1071.10): calcd. C 53.82, H 2.82; found C 53.06, H 2.94. ^{1}H NMR ($CDCl_3$, 293 K): δ = 7.7–7.1 (m, 30 H, Ph) ppm. ^{19}F NMR ($CDCl_3$, 293 K): δ = –89.05 (s, 4 F, F_{ortho}), –120.34 (s, 2 F, F_{para}) ppm.

Synthesis of *trans*-[$Ni(C_6Cl_2F_3)_2(AsCyPh_2)_2$] (3): Prepared as described for **2** but using $AsCyPh_2$ (1.891 g, 6.00 mmol) instead of $AsPh_3$. Yield: 1.323 g (49%). $C_{48}H_{42}As_2Cl_4F_6Ni$ (1083.20): calcd. C 53.22, H 3.91; found C 52.94, H 3.60. ^{1}H NMR ($CDCl_3$, 293 K): δ = 7.4–7.0 (m, 20 H, Ph), 2.11 (m, 2 H, C*H*, Cy), 1.88–0.88 (m, 20 H, Cy) ppm. ^{19}F NMR ($CDCl_3$, 293 K): δ = –88.75 (s, 4 F, F_{ortho}), –120.08 (s, 2 F, F_{para}) ppm.

Synthesis of *trans*-[$Ni(C_6Cl_2F_3)_2(AsMePh_2)_2$] (4): Prepared as described for **2** but using $AsMePh_2$ (1.465 g, 6.00 mmol) instead of $AsPh_3$. Yield: 0.834 g (35%). $C_{38}H_{26}As_2Cl_4F_6Ni$ (946.96): calcd. C 48.20, H 2.77; found C 47.82, H 2.71. ^{1}H NMR ($CDCl_3$, 293 K): δ = 7.31 (m, 20 H, Ph), 1.57 (s, 6 H, Me) ppm. ^{19}F NMR ($CDCl_3$, 293 K): δ = –90.29 (s, 4 F, F_{ortho}), –119.69 (s, 2 F, F_{para}) ppm.

Synthesis of *trans*-[$Ni(C_6Cl_2F_3)_2(PPh_3)_2$] (5): To a solution of PPh_3 (0.0787 g, 0.30 mmol) in $CHCl_3$ (20 mL) solid **1** (0.175 g, 0.15 mmol) was added. After complete dissolution of the nickel compound, the solution was stirred for 30 min, filtered through Celite®, and then the solvent was evaporated to dryness. The solid residue was washed with *n*-hexane (4 × 10 mL) to remove the $SbPh_3$, filtered and vacuum dried. Yield 0.128 g (87%). $C_{48}H_{30}Cl_4F_6NiP_2$ (983.21): calcd. C 58.64, H 3.07; found C 58.31, H 3.00. ^{1}H NMR ($CDCl_3$, 293 K): δ = 7.50 (m, 4 H, Ph), 7.29 (m, 2 H, Ph), 7.19 (m, 4 H, Ph) ppm. ^{19}F NMR ($CDCl_3$, 293 K): δ =

–89.04 (t, $^4J_{\text{P–F}}$ = 2.7 Hz, 4 F, F_{ortho}), –121.21 (t, $^6J_{\text{P–F}}$ = 3.4 Hz, 2 F, F_{para}) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ = 22.4 (m) ppm.

Synthesis of $C_6Cl_2F_3$–$C_6Cl_2F_3$ (6): A solution of **1** (1.400 g, 1.20 mmol) in chloroform (250 mL) was refluxed for 12 h. The resulting brown suspension was evaporated to dryness and the residue was chromatographed (silica gel/hexane). The fraction corresponding to the first eluted compound was evaporated to dryness giving a white solid. Yield: 0.303 g (62%). $C_{12}Cl_4F_6$ (399.93): calcd. C 36.04; found C 36.20. GS-MS: *m/z* = 397.8 $[M]^+$. ^{19}F NMR ($CDCl_3$, 293 K): δ = –107.48 (m, 1 F, F_{para}), –110.78 (m, 2 F, F_{ortho}) ppm.

Synthesis of $C_6Cl_2F_3H$ (7): To a solution of $LiC_6Cl_2F_3$ prepared from $C_6Cl_3F_3$ (1.000 g, 4.25 mmol) and BuLi (4.25 mmol) at –78 °C, was added H_2O (0.300 g, 16.65 mmol). The mixture was allowed to warm to room temperature, dried with $MgSO_4$, and the solvents evaporated to dryness, yielding a colorless oil. Yield: 0.717 g (84%). GS-MS: *m/z* (%) = 199.9 $[M]^+$. ^1H NMR ($CDCl_3$, 293 K): δ = 6.91 (td, $^3J_{\text{H,F}}$ = 8.6 Hz, $^5J_{\text{H,F}}$ = 2.4 Hz, 1 H) ppm. ^{19}F NMR ($CDCl_3$, 293 K): δ = –110.64 (m, 1 F, F_{para}), –112.04 (dd, $^3J_{\text{H,F}}$ = 8.6 Hz, $^4J_{\text{F–F}}$ = 1.8 Hz, 2 F, F_{ortho}) ppm.

Polymerization Experiments: All the polymerization catalysis reactions were carried out under N_2, in Schlenk flasks (25 mL) reacting norbornene with a monomer:catalyst ratio of 2000:1. In a typical experiment norbornene (866.3 mg, 9.2 mmol) was dissolved in deoxygenated CH_2Cl_2 (3 mL). To the stirred solution the solid catalyst (4.9 mg of **2**, 4.6 µmol) was added. The reaction started immediately, giving polynorbornene as a white precipitate (the reaction is better done in a round-bottomed flask, since the heat generated by the reaction makes the solvent boil). The stirring was maintained for 30 min and the reaction mass was poured into MeOH (100 mL). The polymer was filtered, washed several times with MeOH and vacuum dried. Yield: 650 mg (75%). NMR spectroscopic data of the polymers. ^{13}C DEPT NMR spectra ($CDCl_3$) of the polymers were recorded, and in all cases a similar spectra were obtained with broad signals at the following chemical shifts, δ = 54–45 (CH), 45–38 (CH), 38–34 (CH_2), 34–28 (CH_2) ppm.

Experimental Procedure for X-ray Crystallography: Suitable single crystals were mounted in glass fibers, and diffraction measurements were made with a Bruker SMART CCD area-detector diffractometer with Mo-K_α radiation (λ = 0.71073 Å).[32] Intensities were integrated from several series of exposures, each exposure covering 0.3° in ω, the total data set being a hemisphere.[33] Absorption corrections were applied, based on multiple and symmetry-equivalent measurements.[34] The structure was solved by direct methods and refined by least-squares on massed F^2 values for all reflections (see Table 3).[35] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. Hydrogen atoms were taken into account at calculated positions and their positional parameters were refined. Refinement proceeded smoothly to give R_1 = 0.0423 based on the reflections with $I > 2\sigma(I)$ and wR_2 = 0.0965 for all data. Complex neutral-atom scattering factors were used.[36] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications with the following deposition numbers: CCDC-262216, -262215, and -262214 for complexes **1**, **2**, and **5**, respectively. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Supporting Information: Two ORTEP figures for compounds **1** and **2** are provided as Supporting Information (see also the footnote on the first page of this article).

Table 3. Crystal data and structure refinement for **1**, **2** and **5**.

	1	**2**	**5**
Empirical formula	$C_{48}H_{30}Cl_4F_6NiSb_2$	$C_{48}H_{30}As_2Cl_4F_6Ni$	$C_{48}H_{30}Cl_4F_6NiP_2$
Formula mass	1164.73	1071.07	983.17
Temperature	298(2)	298(2) K	293(2) K
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	triclinic
Space group	*P*1	*P*1	*P*1
a [Å]	10.045(3)	10.023(4)	10.062(5)
b [Å]	11.066(3)	11.078(5)	13.769(5)
c [Å]	11.733(3)	11.448(5)	15.780(5)
α [°]	95.747(6)	89.597(8)	86.905(5)
β [°]	112.001(6)	69.929(8)	89.449(5)
γ [°]	103.772(5)	67.957(8)	83.725(5)
V [Å^3]	1148.1(6)	1095.7(8)	2169.9(15)
Z	1	1	2
$D_{\text{calcd.}}$ [g cm^{-3}]	1.685	1.623	1.505
Absorption coefficient [mm^{-1}]	1.864	2.245	0.828
F(000)	570	534	996
Crystal size [mm]	0.16 × 0.06 × 0.03	0.24 × 0.12 × 0.08	0.35 × 0.22 × 0.09
Theta range for data collection	1.91 to 23.31°	1.91 to 23.34°	1.49 to 23.27°
Reflections collected	5374	5185	10214
Independent reflections	3286 (R_{int} = 0.0261)	3139 (R_{int} = 0.0215)	6183 (R_{int} = 0.0197)
Absorption correction	SADABS	SADABS	SADABS
Maximum and minimum transmission factor	1.000000 0.561030	1.000000 0.720972	1.000000 0.823285
Data/restraints/parameters	3286/0/277	3139/0/277	6183/0/551
Goodness-of-fit on F^2	0.946	1.006	1.037
R_1 [$I > 2\sigma(I)$]	0.0347	0.0284	0.0423
wR_2 (all data)	0.0810	0.0779	0.0965

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[1] C. Janiak, P. G. Lassahn, *J. Mol. Catal. A: Chem.* **2001**, *166*, 193–209.

[2] C. Karafilidis, H. Hermann, A. Rufiñska, B. Gabor, R. J. Mynott, G. Breitenbruch, C. Weidenthaler, J. Rust, W. Joppek, M. S. Brookhart, W. Thiel, G. Fink, *Angew. Chem. Int. Ed.* **2004**, *43*, 2444–2446.

[3] B. L. Goodall in *Late Transition Metal Polymerization Catalysis* (Eds.: B. Rieger, L. Saunders Baugh, S. Katcker, S. Striegler), Wiley-VCH, Weinheim, **2003**, chapter 4.

[4] a) M. C. Sacchi, M. Sonzogni, S. Losio, F. Forlini, P. Locatelli, I. Tritto, M. Licchelli, *Macromol. Chem. Phys.* **2001**, *202*, 2052–2058; b) C. Zhao, R. Ribeiro, V. S. Subrahmayam, C. L. Gil, A. P. de Lima, *Polymer* **2001**, *42*, 2455–2462; c) C. Janiak, P.-G. Lasshahn, *Polym. Bull.* **2002**, *47*, 539–546.

[5] S. J. Diamanti, P. Ghosh, F. Shimizu, G. C. Bazan, *Macromolecules* **2003**, *36*, 9731–9735.

[6] B. Y. Lee, Y. H. Kim, H. J. Shin, C. H. Lee, *Organometallics* **2002**, *21*, 3481–3484.

[7] W.-H. Sun, H. Yang, Z. Li, Y. Li, *Organometallics* **2003**, *22*, 3678–3683.

[8] G. M. Benedikt, E. Elce, B. L. Goodall, H. A. Kalamarides, L. H. III McIntosh, L. F. Rhodes, K. T. Selvy, C. Andes, K. Oyler, A. Sen, *Macromolecules* **2002**, *35*, 8978–8988.

[9] D. A. Barnes, G. M. Benedikt, B. L. Goodall, S. S. Huang, H. A. Kalamarides, S. Lenhard, L. H. III McIntosh, K. T. Selvy, R. A. Shick, L. F. Rhodes, *Macromolecules* **2003**, *36*, 2623–2632.

[10] C.-F. Huang, S.-K. Wang, S.-W. Kuo, W.-J. Huang, F.-C. Chang, *J. Appl. Polym. Sci.* **2004**, *92*, 1824–1833.

[11] B. L. Goodall, S. Jayaraman, R. A. Shick, L. F. Rhodes, R. D. Allen, R. A. DiPietro, T. Wallow, *US Patent* **2004**, 6723486.

[12] F. H. Allen, J. E. Davies, J. J. Galloy, D. Johnson, O. Kennard, C. F. Macrae, E. M. Mitcher, G. F. Mitchell, J. M. Smith, D. G. Watson, *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187–204.

[13] K. Herbst, P. Zanello, M. Corsini, N. D′Amelio, L. Dahlenburg, M. Brorson, *Inorg. Chem.* **2003**, *42*, 974–981.

[14] M. Jimenez-Tenorio, M. C. Puerta, I. Salcedo, P. Valerga, S. I. Costa, P. T. Gomes, K. Mereiter, *Chem. Commun.* **2003**, 1168–1169.

[15] a) J. Vicente, A. Arcas, D. Bautista, *Organometallics* **1997**, *16*, 2127–2138; b) J. Vicente, J. A. Abad, A. D. Frankland, M. C. Ramírez de Arellano, *Chem. Eur. J.* **1999**, *5*, 3066–3075; c) J. Vicente, J. A. Abad, E. Martínez-Viviente, P. G. Jones, *Organometallics* **2002**, *21*, 4454–4467; d) J. Vicente, A. Arcas, D. Bautista, M. C. Ramírez de Arellano, *J. Organomet. Chem.* **2002**, *663*, 164–172.

[16] For L–Ni–L angles larger than 100° with L = PPh_3 in planar complexes see for instance: a) S. D. Ittel, J. A. Ibers, *J. Organomet. Chem.* **1973**, *57*, 389–402; b) K. R. Porschke, Y.-H. Tsay, C. Kruger, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 323–324; c) C. Mealli, S. Midollini, S. Moneti, L. Sacconi, J. Silvestre, T. A. Albright, *J. Am. Chem. Soc.* **1982**, *104*, 95–107; d) H. Gorls, B. Schulz, U. Rosenthal, W. Schulz, *Crys. Res. Tecnol.* **1988**, *23*, 25–33; e) R. Countryman, B. R. Penfold, *J. Cryst. Mol. Struct.* **1972**, *2*, 281; f) J. R. Ascenso, A. R. Dias, M. T. Duarte, P. T. Gomes, J. N. Marote, A. F. G. Ribeiro, *J. Organomet. Chem.* **2001**, *632*, 164–174; g) J.-T. Ahlemann, H. W. Roesky, R. Murugavel, E. Parisini, M. Noltemeyer, H.-G. Schmidt, O. Müller, R. Herbst-Irmer, L. N. Markovskii, Y. G. Shermolovich, *Chem. Ber./Recueil* **1997**, *130*, 1113–1121.

[17] a) M. D. Rausch, Y. Tibbetts, *Inorg. Chem.* **1970**, 512–516; b) M. D. Rausch, Y. F. Chang, H. B. Gordon, *Inorg. Chem.* **1969**, 1355–1362.

[18] M. R. Churchill, M. V. Veidis, *J. Chem. Soc. Dalton* **1972**, 670–674.

[19] R. McDonald, K. C. Sturge, A. D. Hunter, L. Shilliday, *Organometallics* **1992**, *11*, 893–900.

[20] J. Forniés, A. Martín, B. Menjón, H. A. Kalamarides, L. F. Rhodes, C. S. Day, V. W. Day, *Chem. Eur. J.* **2002**, *21*, 4925–4934.

[21] T. Yamamoto, M. Abla, Y. Murakami, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1997–2009.

[22] When bonded to a transition metal atom the F_{ortho} signals appear strongly unshielded, while the F_{para} signal is shielded. The chemical shift difference between F_{ortho} and F_{para} is, in metal complexes, about 30–40 ppm while in organic compounds it is about 2–15 ppm. For chemical shifts of $C_6Cl_2F_3$ bonded to carbon see: A. L. Casado, P. Espinet, *J. Am. Chem. Soc.* **1998**, *120*, 8978–8985. For chemical shifts of metal-bonded $C_6Cl_2F_3$ see for instance; a) M. A. Alonso, J. A. Casares, P. Espinet, J. M. Martínez-Ilarduya, C. Pérez-Briso, *Eur. J. Inorg. Chem.* **1998**, 1745–1753; b) J. A. Casares, P. Espinet, K. Soulantica, I. Pascual, A. Guy Orpen, *Inorg. Chem.* **1997**, *36*, 5251–5256.

[23] See for instance: a) A. C. Albeniz, P. Espinet, Y.-S. Lin, *Organometallics* **1997**, *16*, 4138–4144; b) A. C. Albéniz, P. Espinet, Y.-S. Lin, *Organometallics* **1997**, *16*, 5964–5973.

[24] J. Lipian, R. A. Mimna, J. C. Fondran, D. Yandulov, R. A. Shick, B. L. Goodall, L. F. Rhodes, J. C. Huffman, *Macromolecules* **2002**, *35*, 8969–8977.

[25] Manuscript in preparation.

[26] A. D. Hennis, J. D. Polley, G. S. Long, A. Sen, D. Yandulov, J. Lipian, G. M. Benedikt, L. F. Rhodes, J. Huffman, *Organometallics* **2001**, *20*, 2802–2812.

[27] J. K. Funk, C. E. Andes, A. Sen, *Organometallics* **2004**, *23*, 1680–1683.

[28] R. B. King, *Organometallic Syntheses* (Eds.: J. J. Eisch, R. B. King), Academis Press, New York, **1965**, vol. 1, p. 72.

[29] C. A. Bayse, R. L. Luck, E. J. Schelter, *Inorg. Chem.* **2001**, *40*, 3463–3467.

[30] P. Espinet, J. M. Martínez-Ilarduya, C. Pérez-Briso, A. L. Casado, M. A. Alonso, *J. Organomet. Chem.* **1998**, *551*, 9–20.

[31] W. Levason, C. A. McAuliffe, *Inorganic Syntheses* **1976**, *16*, 188–192.

[32] *SMART*, diffractometer control software, Bruker Analytical X-ray Instruments Inc., Madison, WI, Version 5.051, **1998**.

[33] *SAINT*, integration software, Bruker Analytical X-ray Instruments Inc., Madison, WI, Version 6.02, **1999**.

[34] G. M. Sheldrick, *SADABS*, a program for absorption correction with the Siemens SMART system, University of Göttingen, **1996**.

[35] G. W. Sheldrick, *SHELXTL*, Bruker Analytical Instruments, Madison, Version 5.1, **1998**.

[36] International Tables for Crystallography, Kluwer, Dordrecht, **1992**, vol. C.

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