Palladium Catalysts for Norbornene Polymerization. A Study by NMR and Calorimetric Methods

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Received March 23, 2008

Neutral *trans*-[Pd(C_6F_5)XL_2] (X = Cl, Br) and cationic *trans*-[Pd(C_6F_5)L_2(NCMe)]BF_4 (L = $SbPh_3$, $AsPh_3$, As($C_6Cl_2F_3$)Ph_2, $AsCyPh_2$, $AsMePh_2$, PPh_3) complexes have been studied and tested for norbornene (NB) polymerization and copolymerization with 5-norbornene-2-carboxaldehyde (NB-CHO). The neutral complexes are almost inactive and produce only small amounts of oligomers, but the cationic complexes with arsines and stibines are very good for palladium-catalyzed norbornene polymerization. External coordinating molecules (e.g., ligands or monomers with O-donor groups) compete with the olefin function for the coordination sites on Pd and inhibit the reaction. In spite of this, copolymerization of norbornene and 5-norbornene-2-carboxaldehyde could be achieved, with lower yields and higher incorporations of the functionalized norbornene as the NB:NB-CHO ratio decreases. The complex with the fluorinated arsine $AsPh_2(C_6Cl_2F_3)$ is the most active catalyst and allows for easy spectroscopic study of the reacting systems by ^{19}F NMR. Calorimetry provides straightforward monitoring and detection of activation and deactivation processes in polymerization reactions that give insoluble products and cannot be followed by NMR spectroscopy.

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. With norbornene (bicyclo[2.2.1]hept-2-ene) and norbornene derivatives as the starting materials, different classes of polymers can be obtained by selecting polymerization catalysts that drive the reaction via cationic or radical pathways, ring-opening metathesis, or insertion routes (Scheme 1).[1]

Cationic polymerization of norbornene (NB) results in the formation of low-molecular-weight 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-metal metallocenes or with late-transition-metal 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]

Nickel and palladium 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 ethylene and with other functionalized norbornenes.[1,3–17] Usually the polymerization requires a nickel(II) catalyst and an organometallic cocatalyst (typically methylaluminoxane or $B(C_6F_5)_3$),[1,3,4,9,10] but some nickel[10,11] and palladium organometallics are very efficient without cocatalyst. Many of these catalysts are based on chelating ligands, while phosphines are the most often used

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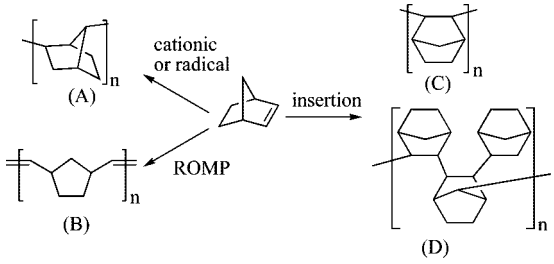
10.1021/om800264a CCC: $40.75
Publication on Web 07/02/2008

Scheme 1



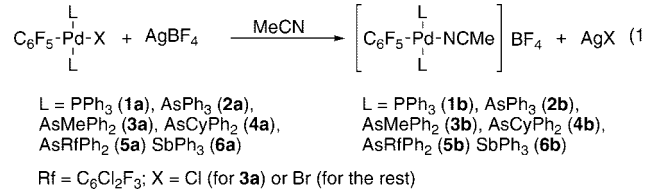
monodentate ligands.[18,19] The use of very bulky monodentate phosphines has proved to be advantageous for controlling the polymerization of functionalized NB.[14]

The ligands used in Ni and Pd catalysis have to fulfill two requirements: they have to stabilize the complex to keep it in solution as an active metal center, but they also have to be weak enough to allow for coordination of the norbornene. Often phosphine ligands are too strongly donating. The weaker As and Sb donor ligands are still able to sufficiently stabilize late-transition-metal organometallic complexes, as we have shown in a recent paper where stable nickel catalysts with As or Sb donor ligands show very high activity in norbornene polymerization.[19] In an independent study it was proven that the As and Sb donor ligands in these complexes are very easily displaced and the complexes are isomerized in acetone solution through a complex system of consecutive substitutions in solution.[20] Taken together, the results of these two studies suggest that the less coordinating ligands (as far as they are sufficiently stabilizing) give rise to the most efficient catalysts. The coordinating ability of the ligands can be tuned through the donor atom ($SbPh_3$ vs $AsPh_3$), by electronic means ($AsPh_3$ vs $AsMePh_2$), and also by steric means ($AsMePh_2$ vs $AsCyPh_2$).

In this paper we report the synthesis of complexes *trans*-$[Pd(C_6F_5)L_2(NCMe)]BF_4$ (L = PPh_3, $AsPh_3$, $AsMePh_2$, $AsCyPh_2$, $As(C_6Cl_2F_3)Ph_2$, $SbPh_3$) and their catalytic activity in the insertion polymerization of norbornene. The polynorbornene produced is highly insoluble. This is a frequent result, particularly common in palladium-catalyzed polymerization of norbornene,[4,11] that imposes serious limitations to GPC characterization and to spectroscopic studies. The latter problem has been mitigated here by using microcalorimetry to monitor the reactions.

Results and Discussion

Synthesis of the Complexes. The cationic complexes *trans*-$[Pd(C_6F_5)L_2(NCMe)]BF_4$ (L = PPh_3, $AsPh_3$, $AsMePh_2$, $AsCyPh_2$, $AsRfPh_2$, $SbPh_3$; Rf = $C_6Cl_2F_3$), were obtained by abstracting the halogen from *trans*-$[Pd(C_6F_5)XL_2]$ with $AgBF_4$ in acetonitrile (eq 1).



Complexes **1b**−**6b** are stable in the solid state and can be stored for long periods. The complexes have been characterized in solution by ^1H, ^{19}F, and ^{13}C NMR and IR spectroscopy. Complexes **3b** and **5b** were also characterized by X-ray diffraction (Figure 1). Table 1 collects relevant bond distances and angles, and Figure 1 shows ORTEP representations of the cations. Both compounds show a square-planar coordination, with angles between adjacent donor atoms fairly close to 90° and the two arsine ligands mutually trans. The Pd−C bond lengths are similar to those found in the Cambridge Structural Database (CSD) for other complexes with the (pentafluorophenyl)palladium moiety. The Pd−As bond lengths are also similar to those found in other *trans*-bis(arsine)palladium complexes, and the Pd−N bond length is within the range found in the CSD for Pd−NCMe bonds. In both complexes the pentafluorophenyl ring is tilted, making angles of 84° (**3b**) and 77° (**5b**) with the coordination plane, lying almost parallel to one phenyl ring of one arsine in **3b**, and being sandwiched by one Ph and one Rf ring (each of one arsine) in **5b**. The Pd−C bonds are equal within experimental error for both complexes, whereas the difference in bond lengths for Pd−$AsRfPh_2$ in **5b** (average 2.414 Å) and Pd−$AsMePh_2$ in **3b** (average 2.401 Å) is significant and probably associated with the poorer donor ability of $AsRfPh_2$ and the different bulks of both ligands. The cone angles, calculated from the X-ray structures as described in the literature,[21,22] are 143° for $AsMePh_2$ and 167° for $AsRfPh_2$.

Polymerization of Norbornene. The polymerization experiments were carried out in CH_2Cl_2 at 25 °C. Under the mild conditions used, the neutral compounds (**1a**−**6a**) and the cationic compound with PPh_3 (**1b**) do not afford a polymer, while the cationic complexes (**2b**−**6b**) are efficient catalysts that produce polynorbornene, which precipitates from the reaction as a white solid. The amount of unreacted norbornene was measured, by GC, on the supernatant liquids after pouring the suspension onto methanol. Attempts to dissolve the polymers in organic solvents (including ethers, chloroform, dichloromethane, 1,2-dichloroethane, chlorobenzene, hot 1,2-dichlorobenzene, and hot 1,2,4-trichlorobenzene) were unsuccessful, which precluded their characterization by GPC.

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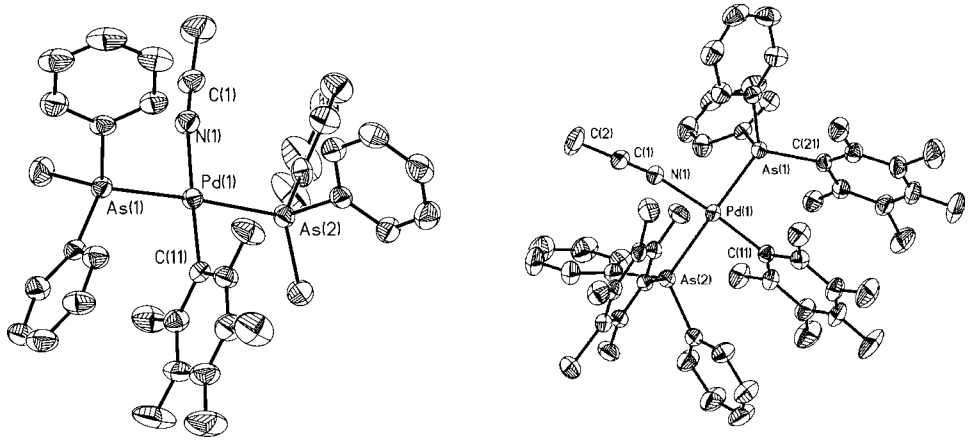


Figure 1. ORTEP diagram of the cations *trans*-$[Pd(C_6F_5)(AsMePh_2)_2(NCMe)]^+$ (**3b**, left) and *trans*-$[Pd(C_6F_5)(AsRfPh_2)_2(NCMe)]^+$ (**5b**, right).

Table 1. Selected Bond Lengths (Å) and Angles (deg)

trans-$[Pd(C_6F_5)(AsMePh_2)_2(NCMe)]BF_4$ (**3b**)		*trans*$[Pd(C_6F_5)(AsRfPh_2)_2(NCMe)]BF_4$ (**5b**)	
Pd(1)−C(11)	1.998(5)	Pd(1)−C(11)	2.001(4)
Pd(1)−N(1)	2.056(5)	Pd(1)−N(1)	2.063(4)
Pd(1)−As(1)	2.4007(18)	Pd(1)−As(1)	2.4129(6)
Pd(1)−As(2)	2.4031(18)	Pd(1)−As(2)	2.4167(6)
C(11)−Pd(1)−As(1)	87.22(14)	C(11)−Pd(1)−As(1)	89.58(10)
N(1)−Pd(1)−As(1)	91.76(12)	N(1)−Pd(1)−As(1)	94.03(9)
C(11)−Pd(1)−As(2)	88.50(14)	C(11)−Pd(1)−As(2)	88.72(10)
N(1)−Pd(1)−As(2)	92.51(12)	N(1)−Pd(1)−As(2)	87.35(9)

Table 2. Polymerization of Norbornene with Catalysts $[Pd(C_6F_5)L_2(NCMe)]BF_4$[a]

cat. (L)	yield (%)[b]	induction time (min)[c]	max rate (10^{-4} M s^{-1})	max cat. efficiency (10^5 g of polymer/((mol of Pd) h))	ligand cone angle Θ_T(L) (deg)[d]
1b (PPh_3)	<2.0				145
2b ($AsPh_3$)	62.8	3.2	2.4	2.9	141
3b ($AsMePh_2$)	21.7	2.8	2.2	2.6	143
4b ($AsCyPh_2$)	83.8	12	1.1	1.3	
5b ($AsRfPh_2$)	100.0	1.1	9.2	11	167
6b ($SbPh_3$)	96.6	0.8	1.2	1.4	142

[a] The reactions of 2.3 mmol of norbornene with 1.15 μmol of catalyst in dichloromethane (total solution volume taken to 4 mL; [NB] = 0.575 M, [complex] = 2.8×10^{-4} M) were performed under isothermal conditions at 25 °C. [b] Calculated with respect to the consumed NB, which was measured by GC. [c] The value given is the time elapsed to reach the maximun rate. For its calculation the curves have been corrected using the dynamic correction provided by the instrument software. [d] Calculated for **3b** and **5b** from the X-ray structures. For structures of **1b**, **2b**, and **6b** see ref 19. The calculated cone angle for PPh_3 is as reported by Tolman.[21]

Table 2 shows the polymerization results. The yields obtained are strongly dependent on the L ligand, being noticeably higher for $AsRfPh_2$, $SbPh_3$, $AsCyPh_2$, and $AsPh_3$ than for $AsMePh_2$ and PPh_3. Apparently the highest yields are obtained with more weakly donating or bulkier ligands, which undergo easier substitution (see below for support of this interpretation). Complex **5b**, bearing a bulky and relatively poorly donating ligand (because of the electron-withdrawing effect of the fluorinated ring), is the most efficient (in terms of yield) and the fastest catalyst. Its activity was tested in separate experiments: In a reaction with the ratio NB:**5b** = 20 000:1, 91% polymerization was produced in 24 h;[23] a reaction using 1.65 g of NB (17.5 mmol) and 1.0 μmol of **5b** in 3 mL of dichloromethane afforded 1.05 g of polymer in 30 min (63.6% yield, conversion 2.1×10^6 g of polymer/((mol of Pd catalyst) h)).

NMR Monitoring of Polymerization Experiments. Neutral Complexes. The reactions of NB with neutral complexes $[Pd(C_6F_5)XL_2]$ do not lead to high-M_w polynorbornene under the reaction conditions used (NB:Pd = 2000:1 in CH_2Cl_2 as solvent, at 25 °C). Since this lack of reactivity could be due to the inability of the NB to coordinate to the palladium center, an experiment with a complex containing a ligand that was easier to substitute ($AsRfPh_2$) was carried out. The reaction of *trans*-$[Pd(C_6F_5)Br(AsRfPh_2)_2]$ (**5a**) with NB was followed by ^{19}F NMR on the C_6F_5 group for the possible insertion reaction, as well as on the fluorinated arsine $AsRfPh_2$ (Rf = 3,5-dichloro-2,4,6-trifluorophenyl) for the possible substitution reaction by NB at the palladium center. The complex was dissolved in $CDCl_3$, and a large excess of NB was added (NB:Pd = 98:1). After 24 h at room temperature the ^{19}F NMR showed only 3% of $AsRfPh_2$ in the form of unreacted starting complex, with 73% of $AsRfPh_2$ appearing as uncoordinated ligand (Figure 2). Hence, it must have been substituted by NB in the coordination sphere of Pd; the remaining 24% of $AsRfPh_2$ appeared coordinated to palladium in one or more unidentified complexes, giving a broad signal. Therefore, the mixture contains complexes with only one or no coordinated arsine ligand. On the other hand, the C_6F_5 signals show that only 3% of the pentafluorophenyl groups remain attached to palladium,[24] while 97% of the groups have added to norbornene ($C-C_6F_5$ groups). Integration of aliphatic versus olefinic signals in ^1H NMR shows that 65% of the starting

(23) A 1.732 g portion of norbornene (18.4 mmol) was dissolved in 6 mL of CH_2Cl_2. To this solution was added 1.16 mg of $[PdC_6F_5(AsC_6Cl_2F_3Ph_2)_2(CH_3CN)]BF_4$. The formation of polynorbornene as a white precipitate started immediately. The solution was stirred for 24 h, and the solid was filtered and washed with EtOH.

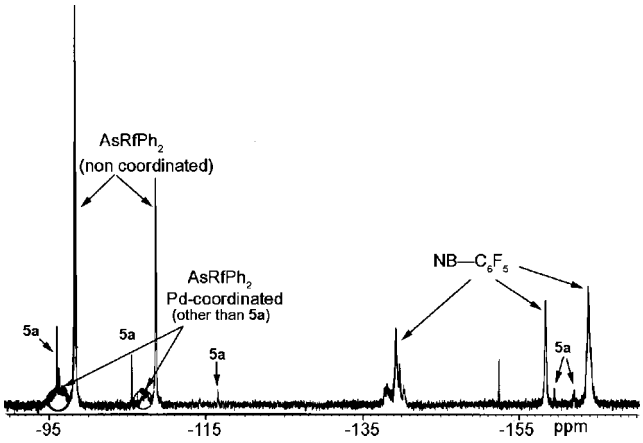


Figure 2. ^{19}F NMR spectrum of a mixture of *trans*-[Pd(C_6F_5)Br($AsRfPh_2$)$_2$] (**5a**) and NB after 24 h of reaction.

norbornene remains unreacted.[25] This NMR experiment shows that, even when NB has doubtlessly coordinated to Pd (NB is the only ligand in the reaction system able to replace the arsine at the palladium center), the reaction on the neutral intermediates formed is slow and is fruitless in terms of high-M_w polymer, leading only to soluble oligomers. In other words, the slow insertion is not due to difficult coordination of the norbornene but to the insertion step itself. The slowness of the insertion reaction observed is in line with reports which suggest that the insertion of olefins into Pd−C bonds is faster for more electrophilic palladium centers.[18b,26]

The same NMR experiment was performed with *trans*-[Pd(C_6F_5)Br($AsPh_3$)$_2$] (**2a**) and norbornene. The reaction was noticeably slower, and after 24 h no significant consumption of norbornene was observed in the ^1H NMR spectrum, although the ^{19}F NMR spectrum indicated that 19% of C_6F_5 groups had added to norbornene (they were detected as C−C_6F_5 groups; this amount is negligible in terms of NB consumption). This noticeable retardation is to be expected, considering that $AsPh_3$ is a better ligand for neutral Pd centers compared to the bulkier and poorer donor $AsRfPh_2$.

Cationic Complexes. The complexes *trans*-[Pd(C_6F_5)L_2(NCMe)]BF_4 are efficient in the production of high-M_w polymer (except for L = PPh_3). In order to know which ligands are displaced by NB under the reaction conditions, complexes **2b** and **5b** were studied by IR spectroscopy to assess whether the acetonitrile remains coordinated or not. Uncoordinated acetonitrile dissolved in $CHCl_3$ gives two bands at 2293 and 2266 cm^{-1},[27] whereas both absorptions appear at higher wavenumbers when the acetonitrile is coordinated to palladium (2323 and 2293 cm^{-1} for complex **2b** and 2324 and 2296 cm^{-1} for complex **5b**). The IR spectrum of a solution of *trans*-[Pd(C_6F_5)($AsPh_3$)$_2$(NCMe)]BF_4 (**2b**) and norbornene (NB:**2b** = 23:1) showed no changes with respect to that of pure **2b**, showing that, at this NB concentration, the ligand-for-norbornene substitution equilibrium is very much shifted toward **2b**.[28] When the same experiment is performed on *trans*-[Pd(C_6F_5)($AsRfPh_2$)$_2$(NCMe)]BF_4 (**5b**) (NB:**5b** = 34:1), a shift of the acetonitrile bands to 2314 and 2285 cm^{-1} is observed, with the complete disappearance of the two bands due to coordinated acetonitrile in **5b**. This shows that a new complex, where the acetonitrile remains coordinated, has been formed; hence, $AsRfPh_2$ is more easily replaced by NB, in cationic complexes, than the harder NCMe or the stronger donor $AsPh_3$. Consistently, the catalyzed polymerization of NB in $CDCl_3$ at 298 K (NB:Pd = 10:1) is faster with *trans*-[Pd(C_6F_5)($AsRfPh_2$)$_2$(NCMe)]BF_4 (**5b**) than with *trans*-[Pd(C_6F_5)($AsPh_3$)$_2$(NCMe)]BF_4 (**2b**).

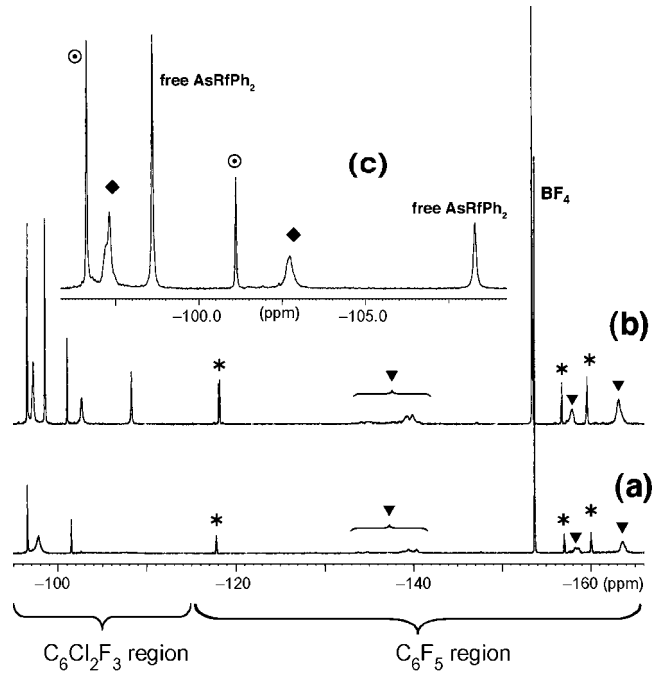


Figure 3. ^{19}F NMR spectra of a $CDCl_3$ solution prepared from NB and *trans*-[Pd(C_6F_5)($AsRfPh_2$)$_2$(NCMe)]BF_4 (**5b**) (NB:Pd = 10:1): (a) at 298 K; (b) at 217 K; (c) expansion of the spectrum at 217 K in the $C_6Cl_2F_3$ range. Legend to symbols: (∗) C_6F_5 in **5b**; (⊙) $AsRfPh_2$ in **5b**; (◆) coordinated $AsRfPh_2$ (other than **5b**); (▼) C_6F_5 attached to a growing polymer chain (all fluorine nuclei; note the narrower range of chemical shifts for C−C_6F_5 compared to Pd−C_6F_5). The $AsRfPh_2$ coordinated to **5b** does not participate in the ligand exchange equilibrium that leads to the coalescence of other $AsRfPh_2$ signals at 298 K.

The ^1H NMR spectrum of a freshly prepared sample (298 K) of *trans*-[Pd(C_6F_5)($AsRfPh_2$)$_2$(NCMe)]BF_4 (NB:Pd = 10:1) does not show olefin signals of noncoordinated NB (6.01 ppm), since it has already coordinated to Pd (a very broad signal at 6.5−6.9 ppm is assigned to coordinated norbornene) or is incorporated into the polymer during the manipulation time. The ^{19}F NMR spectra in the C_6F_5 region shows signals of the starting complex and very broad signals of C−C_6F_5 (Figure 3a). In the $C_6Cl_2F_3$ region very broad signals of $AsRfPh_2$ are observed. Since the signals of the remaining unreacted **5b** are sharp, the broadness is suggestive of an exchange process between $AsRfPh_2$ groups noncoordinated and coordinated to palladium centers that are participating in the polymerization reaction. The ^{19}F NMR spectrum registered at 217 K in the C_6F_5 region (Figure 3b) is similar to that at 298 K and does not show signals

(24) The chemical shifts for C-bonded and Pd-bonded C_6F_5 groups are very different and are clearly identified; see for instance: (a) Albéniz, A. C.; Espinet, P.; Foces-Foces, C.; Cano, F. H. *Organometallics* **1990**, *9*, 1079–1085. (b) Albéniz, A. C.; Espinet, P.; Jeannin, Y.; Philoche-Levisalles, M.; Mann, B. E. *J. Am. Chem. Soc.* **1990**, *112*, 6594–6600. (c) Albéniz, A. C.; Espinet, P. *Organometallics* **1991**, *10*, 2987–2988.

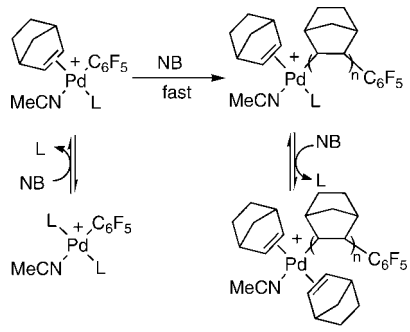
(25) Formation of soluble low-molecular-weight oligomers can explain why no polymer is observed to precipitate in methanol in attempts at polymerization with neutral complexes as catalysts.

(26) Sen, A. *Acc. Chem. Res.* **1988**, *21*, 421–428.

(27) One of the bands is assigned to ν(CN) stretching and the other to a combination band: Storhoff, B. N.; Lewis, H. C. *Coord. Chem. Rev.* **1977**, *23*, 1–29.

(28) The high concentration of palladium complex required to record a IR spectrum precluded the use of an excess of norbornene comparable to the ratio used in the catalytic experiments.

Scheme 2



assignable to complexes of the type $[Pd(C_6F_5)(AsRfPh_2)(NB)(NCMe)]BF_4$ or $[Pd(C_6F_5)(NB)_2(NCMe)]BF_4$. Three groups of signals appear in the $C_6Cl_2F_3$ region: (i) free $AsRfPh_2$, (ii) signals from the starting compound **5b**, and (iii) signals from other palladium-containing $AsRfPh_2$ complex different from **5b**. The last signals are broader than the others at the same temperature, suggesting that they might correspond to palladium complexes containing growing oligomeric polynorbornene chains.

These spectroscopic observations are consistent with the basic sequence of reaction summarized in Scheme 2. The reaction starts with the substitution of an L ligand cis to C_6F_5 by NB, followed by insertion. Then a chain-growing process follows, on intermediates with one or two coordinated NB monomers that have displaced the arsine or stibine ligands. The ligand exchange on complexes that participate in the chain growing is faster than the exchange of free arsine with **5b**, as shown by the NMR spectra at 298 K; this is probably due to the very high trans effect of coordinated NB as compared with the trans effect of arsine (or stibine).

Calorimetric Monitoring of Polymerization. The formation of large amounts of solid or of very viscous solutions precludes spectroscopic monitoring of the polymerization under catalytic conditions. However, the reactions can be properly monitored by calorimetry.[29,30] The calorimeter measures dq/dt (the instantaneous heat flow per time unit, in mJ s^{-1}) at chosen times. At constant pressure, the reaction rate at any instant is proportional to the instantaneous heat flow.[31] The conversion at any instant can be calculated as a quotient between the total heat evolved up to that instant and the total heat evolved when the reaction is complete. As a result, instantaneous concentrations of reactants and products can also be calculated.

The polymerization reactions were monitored in a microcalorimeter. In a standard experiment 2 mL of a dichloromethane solution containing 2.3 mmol of NB was injected in a calorimetric cell containing 2 mL of a solution containing 1.15 μmol of the palladium catalyst in CH_2Cl_2 under nitrogen. When the reaction apparently ceased, 10 mL of methanol was added to fully quench the system, and the content in unreacted NB of the supernatant liquids was measured by GC. Figure 4 shows the reaction rate/time plot for the polymerization experiments. Because it takes time for the heat to flow through the reactor vessel to the sensors in the isothermal block, this raw data curve must be mathematically corrected (see the Experimental Section). In all cases an activation or induction time is observed, during which time the initial complexes form an intermediate, a Pd complex with coordinated norbornene that will undergo insertion. The activation time values given in Table 2 have been taken from the corrected experimental curves, as the time elapsed to reach the maximun rate.

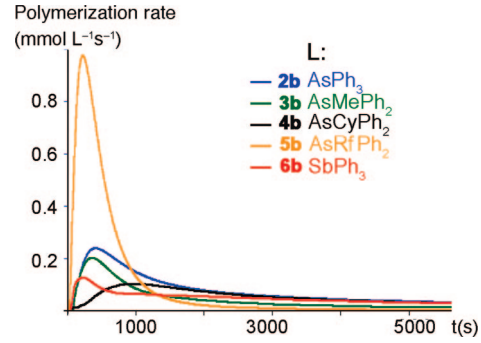


Figure 4. Plot of the polymerization reaction rate (mmol L^{-1} s^{-1}) vs time (s), using **2b**−**6b** as catalyst.

The data collection was maintained until the release of heat ceased, indicating that the reaction had finished. Reaction times between 3 h (for the fastest) and 16 h (for the slowest) were found. For complexes **2b**−**6b** the reaction rate vs norbornene conversion plots give curves, rather than the straight lines expected for a pseudo-first-order rate law,[29e] revealing that a more complex behavior is interfering with the simple first-order behavior. In these plots the reaction rate (the slope of the curves) increases during the activation time and then decreases as catalyst deactivation progresses during the second part of the experiment. As discussed below, this interference corresponds to deactivation of the catalyst. In spite of this complication, which precludes attaining exact kinetic parameters, very valuable information can be obtained from the curves of Figure 4. Large differences in activation time were observed (Table 1). For complex **5b** the maximum rate was reached after 1.1 min, but complex **4b** requires 12 min to reach the maximum. Apparently there is no correlation between activation time and yield of the reaction: complex **3b** has a shorter activation time but a lower yield than **2b** or **4b**. The activation time is short for the complexes with the poorer donor ligands ($AsRfPh_2$, $SbPh_3$), since they are more easily substituted by NB. For stronger ligands ($AsPh_3$, $AsMePh_2$, $AsCyPh_2$; the last ligand might additionally impose severe steric hindrance to associative substitution), the activation energy for L-for-NB substitution is expected to be larger, and the induction time is consistently longer.[32,33]

Because of the activation period and the deactivation process (see below), it is difficult to speak of initial rates, but the curves in Figure 4 allow us to estimate maximum rates for the catalysts, as well as the corresponding maximum catalyst efficiencies.

(29) For the use of calorimetry on catalysis kinetics see for instance: (a) LeBlond, C.; Wang, J.; Larsen, R. D.; Orella, C. J.; Forman, A. L.; Landau, R. N.; Laquidara, J., Jr.; Blackmond, D. G.; Sun, Y.-K. *Thermochim. Acta* **1996**, *289*, 189–207. (b) Singh, U. K.; Strieter, E. R.; Blackmond, D. G.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 14104–14114. (c) Nielsen, L. P. C.; Stevenson, C. P.; Blackmond, D. G.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2004**, *126*, 1360–1362. (d) Zogg, A.; Stoessel, F.; Fischer, U.; Hungerbühler, K. *Thermochim. Acta* **2004**, *419*, 1–17. (e) Blackmond, D. G. *Angew. Chem., Int. Ed.* **2005**, *44*, 4302–4320.

(30) For the use of calorimetry on kinetics of polymerization reactions see: (a) Bechthold, N.; Landfester, K. *Macromolecules* **2000**, *33*, 4682–4689. (b) Karlsson, O. J.; Hassander, H.; Wesslén, B. *J. Appl. Polym. Sci.* **2000**, *77*, 297–311. (c) Saethre, B. *Polym. Int.* **1998**, *45*, 222–228.

(31) For a discussion of the relationship between heat flow and reaction rates see refs 34d,e and the Supporting Information of ref 34c.

(32) Cross, R. J. *Adv. Inorg. Chem.* **1989**, *34*, 219–291.

(33) For associative and dissociative substitution processes in sterically hindered complexes see (a) Bartolomé, C.; Espinet, P.; Martin-Alvarez, J. M.; Villafañe, F. *Eur. J. Inorg. Chem.* **2003**, 3127–3138. (b) Bartolomé, C.; Espinet, P.; Martin-Alvarez, J. M.; Villafañe, F. *Eur. J. Inorg. Chem.* **2004**, 2326–2337.

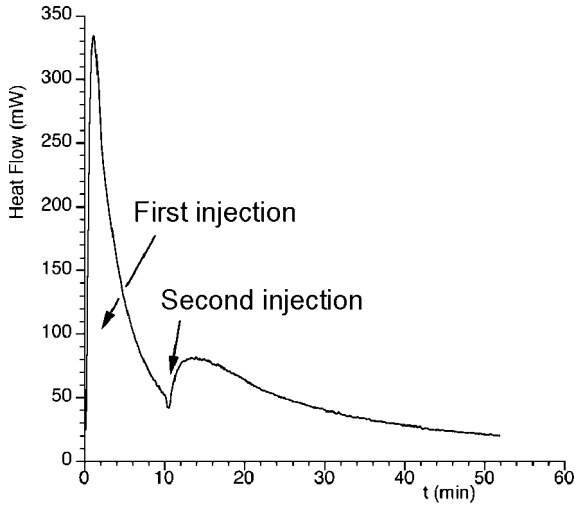


Figure 5. Heat flow vs time plot from the calorimetry experiment in which a second injection of NB is added (catalyst used **5b**; see text for a comprehensive description).

These values are collected in Table 2 and are in the order $AsRfPh_2 > AsPh_3 > AsMePh_2 > SbPh_3 > AsCyPh_2 \gg PPh_3$. The catalyst with the ligand $AsRfPh_2$ is about 4 times faster than the next one.

That a kinetically relevant deactivation process exists, as proposed above, is supported by the effect of adding extra injections of NB to a running reaction mixture. In the experiment shown in Figure 5, an extra amount of NB (2 mL of a CH_2Cl_2 solution containing 2.3 mmol of NB) was injected into a running polymerization of NB (4 mL of a CH_2Cl_2 solution containing 2.3 mmol of NB) using **5b** as catalyst, when the reaction rate had dropped to one-tenth of its maximum value. If deactivation were negligible, a second identical injection of NB should cause the reaction rate to recover to a theoretical value of 260 mW (calculated by correcting for the volume variation with the injection and the remaining unreacted NB). The rate increase was far lower than the expected value.[34] Due to the continuing deactivation the addition of more norbornene to the solution after 150 min did not produce any measurable heat release (that is, any further reaction), showing that the catalyst deactivation at that moment was complete. The deactivation process was further verified by running two polymerizations with the same concentration of catalyst but different concentrations of NB. When the experiment starting with the most concentrated solution in NB reached a concentration in NB identical with that used initially in the diluted experiment, its reaction rate was noticeably lower, supporting that the active catalyst concentration at that moment is noticeably lower than the initial concentration, and a large percentage of the catalyst has been deactivated.[29]

On the other hand, L ligands can compete with NB for the coordination sites at palladium. Consequently, an excess of L (which can be produced if the deactivation of the catalyst occurs with decomposition of the Pd complex) is expected to have a detrimental effect on the catalysis. It has been well studied that, in processes where L substitution precedes the irreversible step, the retarding effect of free L varies from very sharp to negligible and is strongly dependent on the L coordinating ability.[35,36] This

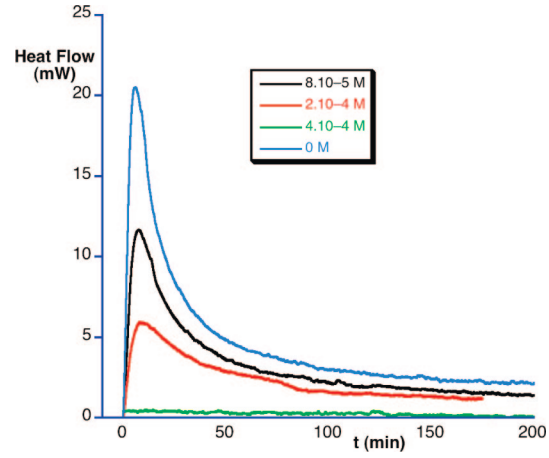


Figure 6. Effect of $[AsPh_3]$ on the polymerization rate. The lines correspond to calorimetric runs of polymerization reactions of NB ([NB] = 0.575 M) catalyzed by **2b** ([**2b**] = 2.88×10^{-4} M), for several concentrations of added $AsPh_3$.

free ligand effect was tested on the polymerization reaction catalyzed with $[PdRf(AsPh_3)_2(CH_3CN)]BF_4$ (**2b**). Increasing concentrations of free $AsPh_3$ produce increasing reduction of the reaction rate (Figure 6). For $AsPh_3$:catalyst = 20:1, the reaction is totally inhibited and no polynorbornene is detected in 24 h.

The evidence suggests that the origin of the observed deactivation is 2-fold: (i) a decrease in active catalyst concentration, mostly by precipitation or coprecipitation of PolyNB—$Pd(MeCN)(L)(NB)^+$ or PolyNB—$Pd(MeCN)(NB)_2^+$ species, and (ii) an increase in concentration of free L in solution, since L is released in these catalyst sequestering reactions. In practice, this means that the positive effect on the polymerization rate of more poorly coordinating ligands has two origins: (i) the more poorly coordinating ligands are more easily substituted by NB and (ii) the rate retardation produced by the release of free L via catalyst decomposition is less for more poorly coordinating ligands.[35] Thus, both effects cooperate in favor of the efficiency of catalysts with more poorly coordinating ligands, which should, however, be weighed against the survival time of the catalytic species.

Norbornene Polymerization in the Presence of O-Donor Groups. Complexes **1b**−**6b** do not catalyze the polymerization of 5-norbornene-2-carboxaldehyde. This is common for functionalized norbornenes, because coordination of the monomer to the metal through the oxygen atom inhibits the reaction.[37–39] In this sense the functionalized monomer acts as an additional ligand (as just discussed for added $AsPh_3$), competing with the double bond for the coordination positions. This could impede

(34) The NB consumed before the second injection is known from the integrated area of the curve.

(35) For instance, to obtain the retarding effect of 2×10^{-4} M of PPh_3, 5×10^{-2} M of $AsPh_3$ is necessary: Casado, A. L.; Espinet, P. *Organometallics* **2003**, *22*, 1305–1309.

(36) See also (a) Albéniz, A. C.; Casado, A. L.; Espinet, P. *Inorg. Chem.* **1999**, *38*, 2510–2515. (b) Casado, A. L.; Espinet, P. *Organometallics* **1998**, *17*, 954–959.

(37) No specific experiments have been performed to differentiate whether the retardation effect is due to the functionalized norbornene, to norbornene units after one or several intramolecular insertions, or to polymers containing O-functionalized norbornene units. Note, however, that simple O-donor solvents also produce a retardation effect; thus, the excess of functionalized norbornene monomer should be able to produce this retardation.[19]

(38) Funk, J. K.; Andes, C. E.; Sen, A. *Organometallics* **2004**, *23*, 1680–1683.

(39) (a) Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303–310. (b) Markies, B.; Kruis, D.; Rietveld, M. H. P.; Verkerk, K. A. N.; Boersma, J.; Kooijman, H.; Lakin, M. T.; Speck, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1995**, *117*, 5263–5274. (c) Delis, J. G. P.; Aubel, P. B.; Vrieze, D.; van Leeuwen, P. W. N. M.; Veldman, N.; Spek, A. L. *Organometallics* **1997**, *16*, 4150–4160.

Table 3. Norbornene and 5-Norbornene-2-carboxaldehyde Copolymerization, Catalyzed with 5b (4.6 μmol), in CH_2Cl_2 (0.6 mL)

NB:NB-CHO[a]	amt of NB (mmol)	amt of NB-CHO (mmol)	yield (%)[b]	$10^{-5}M_w$	M_w/M_n	C=O:C−H[c]
1:1	4.6	4.6	4.6			0.30
2:1	6.1	3.1	10.6	0.38	1.7	0.24
3:1	6.9	2.3	16.6	0.46	2.1	0.21
6:1	7.9	1.3	31.5	1.12	2.4	0.16
9:1	8.3	0.9	43.8	2.18	2.8	0.14

[a] The total amount of monomer is 9.2 mmol. [b] The reactions were quenched with MeOH after 24 h. [c] Ratio of the IR signal integrals in the ranges 1750−1700 cm^{-1} (ν(C=O)) versus 3200−2675 cm^{-1} ($\nu(C_{aliphatic}-H)$). This column gives only a rough relative estimation of the incorporation of 5-norbornene-2-carboxaldehyde in the different copolymers.[40]

Table 4. IR Data for the Polymerization of Norbornene with 2b and 5b

complex (mol/L)	concn of norbornene (mol/L)	ν_{CN} (cm^{-1})[a]	t[b]
2b		2323, 2293	
2b (0.049)	1.13	2320, 2290	1 h
5b		2324, 2296	
5b (0.027)	0.92	2314, 2285	2 min
free MeCN		2293, 2266	

[a] Significant absorption bands. [b] Reaction time.

double-bond coordination for high concentration of the functionalized norbornene, whereas a more dilute concentration of the polar monomer might permit the reaction to occur. In fact, **2b**−**6b** copolymerized 5-norbornene-2-carboxaldehyde (NB-CHO) with NB, giving moderate yields in 24 h. Table 3 shows the results for **5b**. As expected, the yields increased when the NB-CHO:NB ratio was decreased (Table 3).

The GPC chromatograms of the polymerization product show only one peak, suggesting a copolymerization reaction. The IR spectra of the copolymer show an absorption at 1723 cm^{-1} due to the carbonyl group, which allows the evaluation of polar monomer incorporation in the copolymer chain (Table 3). The incorporation of polar monomer decreases when the NB:NB-CHO ratio increases. The results also show a trend to form longer polymeric chains when the yields are higher. This behavior was reported before for neutral nickel catalysts.[19]

Conclusions

The cationic palladium complexes with arsines and stibines are good catalysts for norbornene polymerization. Among them, the complex with the bulk and more poorly donating fluorinated arsine $As(C_6Cl_2F_3)Ph_2$ is by far the most active catalyst and affords interesting rates of polymerization. Moreover, it allows for easy spectroscopic study of the reacting systems by ^{19}F NMR. The positive effect of more poorly coordinating ligands on the polymerization rate has two origins: (i) the more poorly coordinating ligands are more easily substituted by NB, allowing for faster substitution, and (ii) the rate retardation produced by the release of free L via catalyst decomposition is lower for more poorly coordinating ligands.

External coordinating molecules (e.g., ligands or monomers with O-donor groups) inhibit the reaction because they compete with the olefin function for the coordination sites on Pd. In spite of this, it is possible to achieve the copolymerization of norbornene and 5-norbornene-2-carboxaldehyde, with lower yields and higher incorporations of the functionalized norbornene as the NB:NB-CHO ratio decreases.

Finally, microcalorimetry is a useful method for monitoring polymerization reactions that give insoluble products and cannot be followed by NMR, providing straightforward detection of activation and deactivation processes.

Experimental Section

General Methods. All reactions were carried out under N_2, except when otherwise stated. Solvents were dried and distilled under nitrogen using standard methods.[41] The complexes $[Pd(C_6F_5)Br(NCMe)_2]$,[24a] $[Pd_2(C_6F_5)_2(\mu\text{-}Cl)_2(tht)_2]$ (tht = tetrahydrothiophene),[42] $[Pd(C_6F_5)Br(PPh_3)_2]$ (**1a**), $[Pd(C_6F_5)Br(AsPh_3)_2]$ (**2a**), and $[Pd(C_6F_5)Br(SbPh_3)_2]$ (**6a**),[43] $AsBrPh_2$,[19] the ligands $AsMePh_2$[44] and $AsCyPh_2$,[19] and solutions of $LiC_6Cl_2F_3$ were prepared by published methods.[45] Instrumental methods were as in ref 19.

Synthesis of $As(3,5\text{-}C_6Cl_2F_3)Ph_2$. To a solution of $LiC_6Cl_2F_3$ in Et_2O (35 mL), prepared from $C_6Cl_3F_3$ (2.97 g, 12.6 mmol) and BuLi (1.6 M, 12.6 mmol), at −80 °C, was added a solution of $AsBrPh_2$ (3.90 g, 12.6 mmol) in Et_2O (40 mL). After it was stirred for 30 min at −80 °C, the reaction mixture was warmed to room temperature. The flask was open to the air, and a solution of dilute HCl (30 mL) was added. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (3 × 15 mL). The collected organic layers were washed with water (20 mL), dried over anhydrous $MgSO_4$, and filtered. The solvent was removed, affording an oil. After hexanes was added (10 mL), the solution was cooled to −18 °C until crystallization of the product, which was finally filtered and vacuum-dried. Yield: 3.02 g (56%). Anal. Calcd for $C_{18}H_{10}AsCl_2F_3$: C, 50.38; H, 2.33. Found: C, 50.13; H, 2.34. ^1H NMR ($CDCl_3$, 293 K): δ 7.47−7.44 (m, 4H, H_{ortho}), 7.40−7.36 (m, 6H, H_{para} and H_{meta}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 160.27 (Rf), 157.90 (Rf), 157.15 (Rf), 154.55 (Rf), 136.34 (C_{ipso} of Ph), 133.27 (CH of Ph), 129.22 (CH of Ph), 128.98 (CH of Ph). ^{19}F NMR ($CDCl_3$, 293 K): δ −98.5 (s, 2F, F_{ortho}), −108.7 (s, 1F, F_{para}).

Synthesis of $[Pd(C_6F_5)Cl(AsMePh_2)_2]$ (3a). To a solution of $[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(tht)_2]$ (0.3771 g, 0.475 mmol) in CH_2Cl_2 (20 mL) was added $AsMePh_2$ (0.4996 g, 2.046 mmol). The solution was stirred for 30 min, filtered, and vacuum-concentrated to 10 mL. Then hexane (10 mL) was added, and the solution was again concentrated until precipitation of the product. The mixture was cooled to −18 °C to complete crystallization of the desired compound, which was finally filtered and vacuum-dried. Yield: 0.4204 g (56%). Anal. Calcd for $C_{32}H_{26}As_2PdF_5Cl$: C, 48.21; H, 3.29. Found: C, 48.11; H, 3.48. ^1H NMR ($CDCl_3$, 293 K): δ 7.5−7.3 (m, 20H, Ph), 1.98 (s, 6H, CH_3). ^{19}F NMR ($CDCl_3$, 293

(40) Integration of IR signals gives only a rough estimation of the composition. It was used because NMR integration should be based on integration the aliphatic signals versus the aldehydic proton. The latter gives an extremely broad signal. This, along with the large difference in intensity, makes compared integration impossible.

(41) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, U.K., 1988.
(42) Usón, R.; Forniés, J.; Martínez, F.; Tomás, M. *J. Chem. Soc., Dalton Trans.* **1980**, 888–893.
(43) Usón, R.; Forniés, J.; Nalda, J. A.; Lozano, M. J.; Espinet, P.; Albéniz, A. C. *Inorg. Chim. Acta* **1989**, *156*, 251–256.
(44) Bayse, C. A.; Luck, R. L.; Schelter, E. J. *Inorg. Chem.* **2001**, *40*, 3463–3467.
(45) Espinet, P.; Martínez-Ilarduya, J. M.; Pérez-Briso, C.; Casado, A. L.; Alonso, M. A. *J. Organomet. Chem.* **1998**, *551*, 9–20.

K): δ −116.40 (m, 2F, F_{ortho}), −161.17 (t, J = 20 Hz, 1F, F_{para}), −162.91 (m, 2F, F_{meta}).

Synthesis of [Pd(C$_6$F$_5$)Br(AsCyPh$_2$)$_2$] (4a). To a solution of $AsCyPh_2$ (0.2101 g, 0.673 mmol) in Et_2O (20 mL) was added [Pd(C$_6$F$_5$)Br(NCMe)$_2$] (0.1465 g, 0.336 mmol). After the mixture was stirred for 45 min, solvent was removed to 5 mL, and hexane (5 mL) was added to precipitate the product. The mixture was cooled to −18 °C to complete crystallization of **4a**, which was finally filtered and vacuum-dried. Yield: 0.2144 g (65%). Anal. Calcd for $C_{42}H_{42}As_2PdF_5Br$: C, 51.58; H, 4.33. Found: C, 51.29; H, 4.23. ^{1}H NMR ($CDCl_3$, 293 K): δ 7.42 (m, 8H, H_{ortho} of Ph), 7.37−7.28 (m, 12H, H_{para} and H_{meta} of Ph), 2.98 (m, 2H, H_{gem} of Cy), 2.26 (m, 4H of Cy), 1.84−1.71 (m, 8H of Cy), 1.43−1.26 (m, 8H of Cy). ^{19}F NMR ($CDCl_3$, 293 K): δ −115.95 (m, 2F, F_{ortho}), −162.07 (t, J = 20 Hz, 1F, F_{para}), −163.22 (m, 2F, F_{meta}).

Synthesis of [Pd(C$_6$F$_5$)Br(AsRfPh$_2$)$_2$] (5a). This compound was prepared as described for **4a**, but using $AsRfPh_2$ (1.2056 g, 2.810 mmol) and [Pd(C$_6$F$_5$)Br(NCMe)$_2$] (0.5268 g, 1.210 mmol). Yield: 1.3922 g (95%). Anal. Calcd for $C_{42}H_{20}As_2PdF_{11}Cl_4Br$: C, 41.64; H, 1.66. Found: C, 41.46; H, 1.86. ^{1}H NMR ($CDCl_3$, 293 K): δ 7.67 (m, 8H, H_{ortho}), 7.5−7.3 (m, 12H, H_{para} and H_{meta}). ^{19}F NMR ($CDCl_3$, 293 K): δ −96.08 (s, 4F, F_{ortho} $C_6Cl_2F_3$), −105.57 (s, 2F, F_{para} $C_6Cl_2F_3$), −116.57 (m, 2F, F_{ortho} C_6F_5), −159.43 (t, J = 20 Hz, 1F, F_{para} C_6F_5), −161.98 (m, 2F, F_{meta} C_6F_5). ^{13}C DEPT NMR (DEPT = distortionless enhancement by polarization transfer; $CDCl_3$, 293 K): δ 133.40, 131.08, 128.90.

Synthesis of [Pd(C$_6$F$_5$)(PPh$_3$)$_2$(NCMe)]BF$_4$ (1b). To a solution of $AgBF_4$ (0.1631 g, 0.838 mmol) in acetonitrile (15 mL) was added [Pd(C$_6$F$_5$)Br(PPh$_3$)$_2$] (0.7356 g, 0.838 mmol). The solution was stirred for 45 min, filtered through celite, and the solution evaporated to 2 mL. Diethyl ether (15 mL) was added and the colorless solid obtained was filtered and vaccuum-dried. Yield: 0.6923 g (89%). Anal. Calcd for $C_{44}H_{33}BF_9NP_2Pd$: C, 57.08; H, 3.59; N, 1.51. Found: C, 56.94; H, 3.56; N, 1.75. IR (ν(CN) region, Nujol−polyethylene, cm^{-1}): 2327, 2298. ^{1}H NMR ($CDCl_3$, 293 K): δ 7.6−7.4 (m, 30H, Ph), 2.02 (s, 3H, CH_3CN). ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K): δ 133.58 (Ph), 131.95 (Ph), 129.18 (Ph), 127.28 (C_{ipso} of Ph), 1.72 (Me of MeCN). ^{19}F NMR ($CDCl_3$, 293 K): δ −118.09, (m, 2F, F_{ortho}), −153.45 (BF_4), −153.50 (BF_4), −159.97 (t, $^3J_{F-F}$ = 20 Hz, 1F, F_{para}), −161.25 (m, 2F, F_{meta}). ^{31}P NMR ($CDCl_3$, 293 K): δ 24.02 (s, PPh_3).

Synthesis of [Pd(C$_6$F$_5$)(AsPh$_3$)$_2$(NCMe)]BF$_4$ (2b). To a solution of $AgBF_4$ (0.0558 g, 0.287 mmol) in acetonitrile (20 mL) was added [Pd(C$_6$F$_5$)Br(AsPh$_3$)$_2$] (0.2768 g, 0.287 mmol). The solution was stirred for 1 h, filtered through Celite, and evaporated to 4 mL. Isopropyl alcohol (10 mL) was added, and the solvent was again removed to half volume, yielding the product as a colorless solid that was filtered and vacuum-dried. Yield: 0.2076 g (71%). Anal. Calcd for $C_{44}H_{33}As_2BF_9NPd$: C, 52.13; H, 3.28; N, 1.38. Found: C, 51.79; H, 3.34; N, 1.72. IR (ν(CN) region, Nujol−polyethylene, cm^{-1}): 2323, 2293. ^{1}H NMR ($CDCl_3$, 293 K): δ 7.6−7.3 (m, 30H, Ph), 1.79 (s, 3H, MeCN). ^{13}C NMR DEPT ($CDCl_3$, 293 K): δ 132.95 (Ph), 131.47 (Ph), 129.75 (Ph). ^{19}F NMR ($CDCl_3$, 293 K): δ −116.98, (m, 2F, F_{ortho}), −153.25 (BF_4), −153.30 (BF_4), −158.86 (t, $^3J_{F-F}$ = 20.1 Hz, 1F, F_{para}), −161.04 (m, 2F, F_{meta}).

Synthesis of [Pd(C$_6$F$_5$)(AsMePh$_2$)$_2$(NCMe)]BF$_4$ (3b). To a solution of $AgBF_4$ (0.0768 g, 0.394 mmol) in acetonitrile (20 mL) was added [Pd(C$_6$F$_5$)Cl(AsMePh$_2$)$_2$] (0.3145 g, 0.394 mmol). The solution was stirred for 30 min, filtered through Celite, and evaporated to dryness. The residue was stirred vigorously with diethyl ether (8 mL), yielding a colorless solid that was filtered and vaccuum-dried. Yield: 0.2616 g (75%). Anal. Calcd for $C_{34}H_{29}As_2BF_9NPd$: C, 45.90; H, 3.29; N, 1.57. Found: C, 45.89; H, 3.37; N, 1.93. IR (ν(CN) region, Nujol−polyethylene, cm^{-1}): 2323, 2295. ^{1}H NMR ($CDCl_3$, 293 K): δ 7.44 (m, 20H, Ph), 1.99 (s, 9H, methyl groups of $AsMePh_2$ and MeCN). ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K): δ 131.95 (Ph), 131.55 (C_{ipso} of Ph), 131.31 (C_{para} of Ph), 129.73 (Ph), 9.99 (CH_3 of $AsMePh_2$), 2.91 (CH_3 of MeCN). ^{19}F NMR ($CDCl_3$, 293 K): δ −116.44 (m, 2F, F_{ortho}), −152.81 (BF_4), −152.86 (BF_4), −157.86 (t, $^3J_{F-F}$ = 19.9 Hz, 1F, F_{para}), −160.95 (m, 2F, F_{meta}).

Synthesis of [Pd(C$_6$F$_5$)(AsCyPh$_2$)$_2$(NCMe)]BF$_4$ (4b). To a solution of $AgBF_4$ (0.0366 g, 0.188 mmol) in acetonitrile (15 mL) was added [Pd(C$_6$F$_5$)Br(AsCyPh$_2$)$_2$] (0.1839 g, 0.188 mmol). The solution was stirred for 2 h, filtered through Celite, and evaporated to dryness. The residue was stirred vigorously with diethyl ether (4 mL), giving a colorless solid that was filtered and vacuum-dried. Yield: 0.1309 g (68%). Anal. Calcd for $C_{44}H_{45}As_2BF_9NPd$: C, 51.51; H, 4.42; N, 1.37. Found: C, 51.90; H, 4.54; N, 1.38. IR (ν(CN) region, Nujol−polyethylene, cm^{-1}): 2321, 2291. ^{1}H NMR ($CDCl_3$, 293 K): δ 7.5−7.3 (m, 20H, Ph), 2.76 (m, 2H, H_{gem} of Cy), 2.12 (s, 3H, H of MeCN), 2.02 (m, 4H of Cy), 1.8−1.6 (m, 4H of Cy), 1.5−1.3 (m, 4H of Cy). ^{13}C NMR DEPT ($CDCl_3$, 293 K): δ 133.04 (CH of Ph), 131.49 (CH_{para} of Ph), 129.52 (CH of Ph), 41.64 (CH_{gem} of Cy), 30.82 (CH_2 of Cy), 27.99 (CH_2 of Cy), 26.15 (CH_2 of Cy), 3.07 (CH_3 of MeCN). ^{19}F NMR ($CDCl_3$, 293 K): δ −115.66 (m, 2F, F_{ortho}), −152.87 (BF_4), −152.92 (BF_4), −158.71 (t, $^3J_{F-F}$ = 20.1 Hz, 1F, F_{para}), −161.27 (m, 2F, F_{meta}).

Synthesis of [Pd(C$_6$F$_5$)(AsRfPh$_2$)$_2$(NCMe)]BF$_4$ (5b). To a solution of $AgBF_4$ (0.2124 g, 1.091 mmol) in acetonitrile (50 mL) was added [Pd(C$_6$F$_5$)Br(AsRfPh$_2$)$_2$] (1.3216 g, 1.091 mmol). The solution was stirred for 1 h, filtered through Celite, and evaporated to dryness. The residue was stirred vigorously with diethyl ether (10 mL), giving a colorless solid that was filtered and vacuum-dried. Yield: 0.9852 g (72%). Anal. Calcd for $C_{44}H_{23}As_2BCl_4F_{15}NPd$: C, 41.96; H, 1.84; N, 1.11. Found: C, 41.64; H, 2.07; N, 1.09. IR (ν(CN) region, Nujol−polyethylene, cm^{-1}): 2324, 2296. ^{1}H NMR ($CDCl_3$, 293 K): δ 7.6−7.4 (m, 20H, Ph), 1.82 (s, 3H, CH_3CN). ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K): δ 131.93 (Ph), 131.79 (Ph), 129.94 (Ph), 127.95 (Ph), 2.30 (CH_3 of MeCN). ^{19}F NMR ($CDCl_3$, 293 K): δ −96.56 (s, 4F, F_{ortho} of $C_6Cl_2F_3$), −101.44 (s, 2F, F_{para} of $C_6Cl_2F_3$), −117.90 (d, J_{F-F} = 22.9 Hz, 2F, F_{ortho} of C_6F_5), −153.44 (s, 4F, BF_4), −153.49 (s, 4F, BF_4), −157.04 (t, $^3J_{F-F}$ = 20.3 Hz, 1F, F_{para} of C_6F_5), −160.07 (t, $^3J_{F-F}$ = 20.3 Hz, 2F, F_{meta} of C_6F_5).

Synthesis of [Pd(C$_6$F$_5$)(SbPh$_3$)$_2$(NCMe)]BF$_4$·0.5CH$_2$Cl$_2$ (6b). To a solution of $AgBF_4$ (0.2845 g, 1.461 mmol) in acetonitrile (15 mL) was added [Pd(C$_6$F$_5$)Br(SbPh$_3$)$_2$] (1.5484 g, 1.461 mmol). The solution was stirred for 1 h, filtered through Celite, and evaporated to 5 mL. Diethyl ether (15 mL) was added, and the colorless solid obtained was filtered and vacuum-dried. Yield: 1.2129 g (75%). Anal. Calcd for $C_{44.5}H_{34}Sb_2BClF_9NPd$: C, 46.76; H, 2.96; N, 1.21. Found: C, 46.71; H, 3.14; N, 1.15. IR (ν(CN) region, Nujol−polyethylene, cm^{-1}): 2326, 2296. ^{1}H NMR ($CDCl_3$, 293 K): δ 7.6−7.3 (m, 30H, Ph), 2.11 (s, 3H, CH_3CN). ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K): δ 135.36 (Ph), 131.43 (C_{para}, Ph), 130.10 (Ph), 127.65 (C_{ipso}, Ph), 3.09 (CH_3 of MeCN). ^{19}F NMR ($CDCl_3$, 293 K): δ −112.66 (m, 2F, F_{ortho}), −153.07 (BF_4), −153.12 (BF_4), −157.54 (t, J = 19 Hz, 1F, F_p), −160.51 (m, 2F, F_{meta}).

Polymerization Experiments. Experiments in NMR Tubes. (a) Reaction of Norbornene with [Pd(C$_6$F$_5$)Br(AsPh$_3$)$_2$]. To a solution of norbornene (64.0 mg, 0.68 mmol) in $CDCl_3$ (0.5 mL) was added [Pd(C$_6$F$_5$)Br(AsPh$_3$)$_2$] (**2a**; 6.6 mg, 6.8 μmol). ^{1}H and ^{19}F NMR spectra were recorded after 1 day at room temperature.

(b) Reaction of Norbornene with [Pd(C$_6$F$_5$)Br(AsRfPh$_2$)$_2$]. To a solution of norbornene (154.0 mg, 1.64 mmol) in $CDCl_3$ (0.5 mL) was added [Pd(C$_6$F$_5$)Br(AsRfPh$_2$)$_2$] (**5a**; 20.3 mg, 16.8 μmol). ^{1}H and ^{19}F NMR spectra were recorded after 1 day at room temperature.

(c) Reaction of Norbornene with *trans*-[Pd(C$_6$F$_5$)(AsRfPh$_2$)$_2$(NCMe)]BF$_4$ (5b). To a solution of norbornene (20.3 mg, 0.216 mmol) in $CDCl_3$ (0.5 mL) was added *trans*-[Pd(C$_6$F$_5$)(AsRfPh$_2$)$_2$(NCMe)]BF$_4$ (**5b**) (27.3 mg, 21.7 μmol). The ^{1}H and ^{19}F NMR spectra at room temperature were then recorded, followed by the

217 K spectra.[46] ^{1}H NMR ($CDCl_3$, 293 K): δ 7.7−7.3 (m, Ph), 6.9−6.5 (b), 3.4−3.1 (b), 3.1−2.8 (b), 2.8−0.7 (a, poly-NB). ^{19}F NMR ($CDCl_3$, 293 K): δ −96.56 (s, F_{ortho} of Rf, **5b**), −97.81 (a, F_{ortho} of Rf in **5b′** and free $AsRfPh_2$), −101.54 (s, F_{para} of Rf in **5b**), −102 to −110 (a, F_{para} of Rf in **5b′** and free $AsRfPh_2$), −117.89 (d, J = 24 Hz, F_{ortho} of C_6F_5 in **5b**), −133 to −135 (a, F_{ortho} of inserted C_6F_5), −136 to −141 (a, F_{ortho} of inserted C_6F_5), −153.72 (s, BF_4), −153.77 (s, BF_4), −157.06 (t, J = 20 Hz, F_{para} of C_6F_5 in **5b**), −157.73 (a, F_{para} of inserted C_6F_5), −160.08 (t, J = 21 Hz, F_{meta} of C_6F_5), −163.65 (a, F_{meta} of inserted C_6F_5). ^{1}H NMR ($CDCl_3$, 217 K): δ 7.7−7.3 (m, Ph), 6.9−6.5 (b), 3.3−3.1 (b), 3.1−2.8 (b), 2.8−0.6 (a, poly-NB). ^{19}F NMR ($CDCl_3$, 217 K): δ −96.64 (s, F_{ortho} of Rf in **5b**), −97.33 (a, F_{ortho} of Rf in **5b′**), −98.61 (s, F_{ortho} of Rf in free $AsRfPh_2$), −101.11 (s, F_{para} of Rf in **5b**), −102.74 (a, F_{para} of Rf in **5b′**), −108.29 (s, F_{para} of Rf in free $AsRfPh_2$), −118.20 (d, J = 24 Hz, F_{ortho} of C_6F_5 in **5b**), −133to −136 (a, F_{ortho} of inserted C_6F_5), −136 to −138 (a, F_{ortho} of inserted C_6F_5), −138 to −141 (a, F_{ortho} of inserted C_6F_5), −153.35 (s, BF_4), −153.40 (s, BF_4), −156.70 (t, J = 20 Hz, F_{para} of C_6F_5 in **5b**), −157.84 (a, F_{para} of inserted C_6F_5), −159.58 (t, J = 21 Hz, F_{meta} of C_6F_5), −163.15 (a, F_{meta} of inserted C_6F_5).

Calorimetric Experiments: Polymerization of Norbornene with $[Pd(C_6F_5)L_2(NCMe)]BF_4$. In a typical calorimetry experiment, a solution of $[Pd(C_6F_5)(AsRfPh_2)_2(NCMe)]BF_4$ (1.453 mg, 1.15 μmol) in CH_2Cl_2 (2 mL) was placed in the reaction cell, while CH_2Cl_2 (2 mL) alone was placed in the reference cell. After the system reached thermal equilibrium, a norbornene solution (1.15 M in CH_2Cl_2, 2 mL, 2.3 mmol) was added to each cell.[47] When the reaction had apparently finished, 10 mL of methanol was added to quench the reaction, and the concentration of unreacted NB was measured in the supernatant liquids by GC. The same procedure was applied to the reactions with the rest of the cationic complexes $[Pd(C_6F_5)L_2(NCMe)]BF_4$ (L = PPh_3, $AsPh_3$, $AsMePh_2$, $AsCyPh_2$, $SbPh_3$).

The reaction was monitored by measuring the heat flow from the sample vessel every 3 s to produce the data curve.

IR Analysis of the Polymerization Reaction of Norbornene with *trans*-$[Pd(C_6F_5)(AsPh_3)_2(NCMe)]BF_4$ (2b) and *trans*-$[Pd(C_6F_5)(AsRfPh_2)_2(NCMe)]BF_4$ (5b). Experiments were carried out at room temperature in $CHCl_3$ solution. Data are given in Table 4.

Copolymerization Experiments of Norbornene with 5-Norbornene-2-carboxaldehyde. In a typical experiment, *trans*-$[Pd(C_6F_5)(AsRfPh_2)_2(NCMe)]BF_4$ (**5b**; 5.8 mg, 4.6 μmol) was added to a solution in CH_2Cl_2 (0.6 mL) of norbornene (4.6 mmol) and 5-norbornene-2-carboxaldehyde (4.6 mmol). The mixture was stirred for 24 h. The mixture was then poured over methanol (50 mL). The copolymer was obtained as a colorless solid that was filtered and vacuum-dried at 25 °C for several hours. The same reaction was carried out with different ratios of the monomers, as indicated in Table 3.

Acknowledgment. Financial support by the Ministerio de Educación y Ciencia (Project No. CTQ2007-67411/BQU), Project INTECAT Consolider Ingenio 2010 (No. CSD2006-0003), and the Junta de Castilla y León (No. VA044A07) is gratefully acknowledged.

Supporting Information Available: Text and tables giving the experimental procedure for X-ray crystallography and crystal data and structure refinement details for for **3b** and **5b** and CIF files giving crystallographic data for **3b** and **5b.** This material is available free of charge via the Internet at http://pubs.acs.org.

OM800264A

(46) Signals assigned to **25′** arise from complexes in which the C_6F_5 group has undergone insertion. $C_6Cl_2F_3$ (Rf) signals assigned to **25′** arise from a cationic complex of the type $[Pd\{(poli\text{-}NB)\text{-}C_6F_5\}(NB)(AsRfPh_2)(NCMe)]^+$. The C_6F_5 signals arise from $[Pd\{(poly\text{-}NB)\text{-}C_6F_5\}(NB)(AsRfPh_2)(NCMe)]^+$ and $[Pd\{(poly\text{-}NB)\text{-}C_6F_5\}(NB)_2(NCMe)]^+$.

(47) Dilution heat of complexes was found to be negligible in our case.