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γ-Agostic Species as Key Intermediates in the Vinyl Addition Polymerization of Norbornene with Cationic (allyl)Pd Catalysts: Synthesis and Mechanistic Insights

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Abstract: Several cationic (allyl)Pd(II) complexes were synthesized and shown to be highly active for (2,3)-vinyl addition polymerization of norbornene (NB) to yield polymers with low molecular weight distributions (MWDs) ranging from 1.2−1.4. Despite the low MWDs, slow initiation was followed by rapid propagation preventing molecular weight control of the poly(norbornene). Several intermediates in these polymerizations initiated with $[(2\text{-R-allyl})\text{Pd}(\text{mesitylene})]^+$ complexes were fully characterized (NMR and X-ray diffraction). Consistent with previous observations the allyl and NB units couple in cis-exo fashion to yield a σ,π-complex capped by mesitylene. Mesitylene is readily displaced by NB to form an agostic intermediate in which NB acts as a bidentate ligand and binds to the cationic Pd center via the π-system and a γ-agostic interaction with the syn hydrogen at C7. The identity of this complex was established by NMR spectroscopy and single-crystal X-ray diffraction. It is significant since it suggests bidentate binding of NB in the propagating species, which cannot be observed by NMR spectroscopy. The NMR studies suggest that the second insertion, i.e., insertion of NB in the agostic intermediate, is the slow initiation step and the subsequent insertions are extremely fast. Therefore, slow chelate opening is the major limitation preventing a living polymerization. This hypothesis was explored using a series of cationic substituted π-allyl complexes; significantly increased reactivity was observed when electron-withdrawing groups were introduced into the allyl moiety. However, despite these modifications initiation remained slow relative to chain propagation.

Introduction

Intensive research efforts have been devoted to the polymerization of cyclic olefins mainly motivated by the useful properties of the resulting materials which include high glass transition temperatures, high optical transparency, low dielectric constants, and low birefringence. Various classes of polymers may be obtained from norbornene (NB, bicyclo[2.2.1]hept-2-ene) and its derivatives by a suitable choice of catalysts that operate via ring-opening metathesis polymerization (ROMP), cationic or radical polymerization, and vinyl addition polymerization.[1−4] A disadvantage of ROMP-derived poly(norbornene) is the unsaturation in the backbone which makes hydrogenation or vulcanization of the polymer necessary for some applications.[5] Cationic and radical polymerizations normally provide low-molecular-weight polymers which incorporate rearranged NB units.[6] Vinyl addition polymerization circumvents both problems and yields a completely saturated high-molecular-weight polymer with no rearranged NB units. Thus coordination−insertion polymerization of NB and NB derivatives has been examined by many groups, and a number of catalysts based on early and late transition metals have emerged. Addition of cocatalysts (usually methylaluminoxane (MAO) or $B(C_6F_5)_3$) is often required for most early and late transition metal complexes. However, late metal nickel and palladium complexes have been reported which do not require cocatalyst addition.[2−4] Included in this category are cationic "naked"-type nickel or palladium complexes or multicomponent systems able to generate similar species, neutral nickel or palladium complexes bearing highly electrophilic groups, and cationic palladium complexes.[7] In this context the cationic "ligandless" $[(\text{allyl})\text{M}(\text{COD})][\text{PF}_6]$ (M = Ni or Pd) systems are the most active catalysts for NB polymerization to date. However, NMR studies revealed a major problem of this catalyst system: polymer was rapidly formed on exposure of NB to the catalyst, but only very little catalyst was consumed, indicating a slow initiation step

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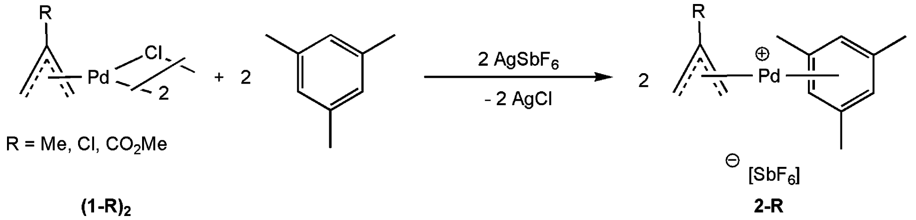
10.1021/ja9025598 CCC: $40.75

Scheme 1



followed by very rapid propagation. This is also reflected in the lack of molecular weight control and the very broad molecular weight distributions (MWDs) for the poly(norbornene) polymers synthesized by these catalysts ranging from 2 to 3. Despite the fact that no spectroscopic information on the "naked" Ni(II)/Pd(II) active species is available, it was suggested to contain only the growing polymer chain and two NB monomers. While the high activity Ni system prevented the detection of any intermediates, the first insertion product was observed for the analogous Pd system[1] in which the Pd−C allyl bond had added in cis-exo fashion across the double bond of NB, consistent with earlier observations by Hughes and Powell.[8] These observations highlighted an important challenge, namely the development of ligandless catalysts in which initiation is rapid and molecular weight can be controlled. Under these conditions, the structure of the propagating species might also be discerned.

More recently, two cationic Pd complexes have been introduced which appear to catalyze the polymerization of NB or NB derivatives in a controlled manner. The cationic $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ complex generates poly(norbornene) with MWDs of 1.07−1.34 and M_n of 11 000−36 000 g mol^{-1}.[9] However, the mechanistic details, e.g., the catalytic active species, are not very well established and the insensitivity of this catalytic system to water addition suggests that an in situ generated cationic "Pd−H" intermediate as the initiating species. The other example is $(^t\text{Bu}_3\text{P})\text{Pd}(\text{Me})(\text{Cl})$ which, on addition of 1 equiv of $\text{NaB}(\text{Ar}_\text{F})_4$, forms the cationic bimetallic species $\{[(^t\text{Bu}_3\text{P})(\text{Me})\text{Pd}]_2(\mu\text{-Cl})\}\{\text{B}(\text{Ar}_\text{F})_4\}$ that polymerizes NB and functionalized NBs.[10−12] Although the low solubility of poly(norbornene) prevented the determination of its molecular weight, it is noteworthy that in this case decreased catalyst loading results in a dramatic increase in apparent turnover frequency, arguing for slow initiation followed by rapid propagation.[10] However, a living polymerization was achieved for the more soluble polymers derived from the methyl ester of norbornene carboxylic acid with M_n's reaching 12 000 g mol^{-1} at 0.86 mol % catalyst loading and a MWD of 1.2.[10]

We have recently reported the synthesis and NB polymerization activity of $[(2\text{-R-allyl})\text{Ni}(\text{mesitylene})]^+$ complexes.[13,14] For these complexes the only detectable polymerization intermediate fully characterized (by NMR and X-ray diffraction) is the first insertion product in which the allyl and NB units couple readily in a cis-exo fashion to yield a σ,π-complex capped by mesitylene. However, NMR studies showed that this coupling event is reversible and also suggested that the second insertion is the slow initiation step, while propagation following the second insertion is extremely fast, preventing a living polymerization. One of the reasons for the slow second insertion may be attributed to slow mesitylene displacement.[14] In order to overcome this limitation we investigated the analogous $[(2\text{-}R\text{-allyl})\text{Pd}(\text{mesitylene})]^+$ complexes in which the mesitylene ligand is very labile and can readily be displaced by other arenes, olefins, and alkynes.[13] The reactivity of these Pd catalysts in NB polymerization is reported herein.

Results and Discussion

Catalyst Preparation. Complex **2-Cl** has been reported previously,[13] and complex **2-CO$_2$Me** was prepared following a similar procedure (Scheme 1, see Experimental Section for details).

Complex **(3-Me)$_2$** is an excellent starting material for the synthesis of compounds **4-Me** and **5-Me**, and it is readily prepared by heating a benzene solution of **(1-Me)$_2$** to 50 °C overnight in the presence of NB to yield colorless crystals of **(3-Me)$_2$** (Scheme 2).[15] A single crystal X-ray diffraction study of **(3-Me)$_2$** confirmed coupling of NB to the allyl fragment in cis-exo fashion, as was also observed for [(2-*R*-allyl)Pd(hfacac)] (hfacac = hexafluoroacetylacetonato) complexes[8] and **(3-H)$_2$**.[16] Selected bond distances for **(3-Me)$_2$** are given in the figure caption (Figure 1) and they compare well to those reported for **(3-H)$_2$**.[16] While **(3-Me)$_2$** is only slightly soluble in chlorinated hydrocarbons such as CHCl_3 and CH_2Cl_2, it is moderately soluble in pyridine and forms a monomeric, neutral pyridine adduct 3-Me(py). Metathesis of **(3-Me)$_2$** with AgSbF_6 in the presence of pyridine or mesitylene yields **4-Me** and **5-Me**, respectively. Both molecules have been characterized by various NMR techniques and X-ray crystallography (Figures 2 and 3). Selected bond distances are given in the figure captions (see Supporting Information for details). Note the significant ring-slippage of the mesitylene ligand in **5-Me** from idealized η^6-coordination (Pd−C$_\text{arene}$ range of distances: 2.450(6)−2.677(6) Å) which is observed for the analogous Ni complex (Ni−C$_\text{arene}$ range of distances: 2.149(6)−2.293(6) Å). This might rationalize the lability of mesitylene with respect to exchange with excess of mesitylene, other arenes and ethers. No reversible C−C bond formation was observed for **(3-Me)$_2$**, **4-Me**, or **5-Me** in contrast to their analogue Ni complexes[14] which might be due to reduced steric strain compared to their Ni congeners.

Polymerizations Results. The cationic Pd complexes described above have been investigated with respect to NB polymerization (Chart 1), and the results are summarized in Tables 1−4.

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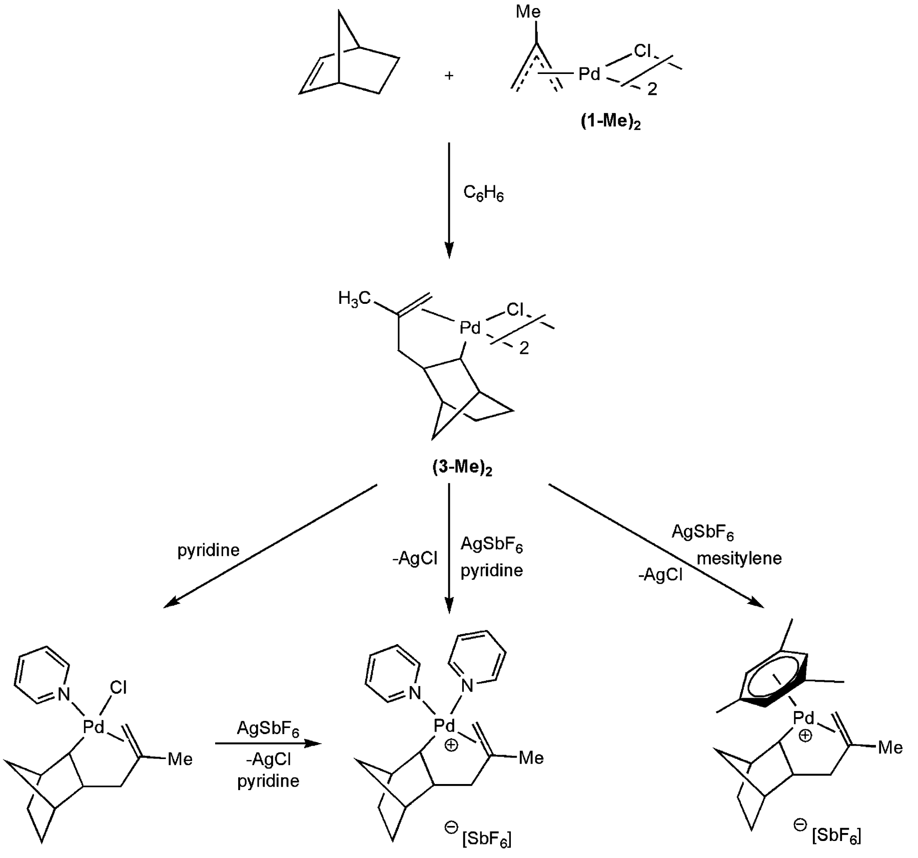
Scheme 2



3-Me(py) **4-Me** **5-Me**

All catalysts exhibit good to high activity in the polymerization of NB. In addition, low MWDs ranging from 1.2 to 1.4 were obtained independent of conversion, but unfortunately, the molecular weight is observed to be nearly independent of conversions and the M_n is larger than expected for living polymerization based on the moles monomer/moles catalyst ratio, e.g., a ratio of 200:1 should give polymer with an M_n of ca. 20 000 g mol^{-1} at 100% conversion. These observations indicate that the investigated catalyst systems suffer from slow initiation and rapid propagation, and only a small percentage of the catalyst is active for polymerization. However, the catalyst reactivity can be ordered in the following manner: **2-Cl** > **2-CO$_2$Me** ≫ **4-Me** ≈ **5-Me**. Most apparent is the fact that the catalyst bearing electron-withdrawing groups (R = Cl and CO$_2$Me) exhibit higher activity than the system with an electron-donating substituent (R = Me). This implies a more rapid initiation for **2-Cl** and **2-CO$_2$Me** compared to **4-Me** and **5-Me** since after 2−3 insertions all species should show the same propagating species. Considering that previous studies in our laboratory have shown that the mesitylene displacement in **2-R** (R = H, Me and Cl) was rapid when exposed to olefins and alkynes,[13] we decided to investigate the reason for the substantial

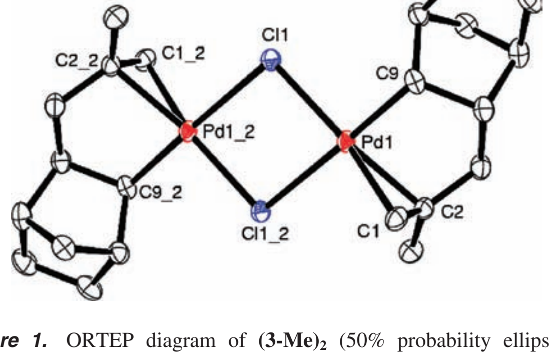


Figure 1. ORTEP diagram of **(3-Me)₂** (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Pd1−C1 2.152(3), Pd1−C2 2.187(3), Pd1−C9 2.042(3), Pd1−C l1 2.3754(8), Pd1−Cl_2 2.5793(8). Atoms with labels bearing "_2" are generated by the symmetry operation: −*x*, −*y*, −*z*.

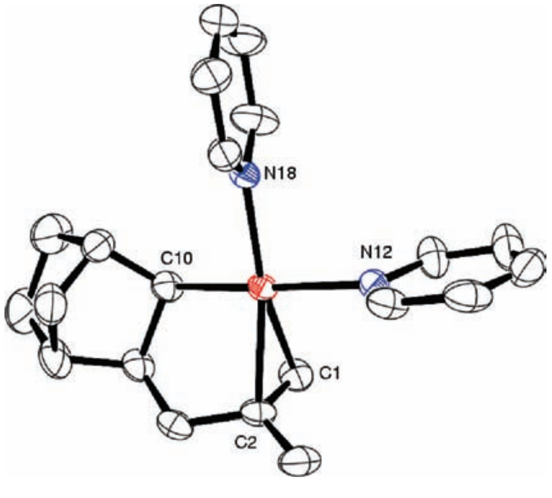


Figure 2. ORTEP diagram of the first insertion product **4-Me** (50% probability ellipsoids). Hydrogen atoms and the [SbF$_6$]$^-$ anion have been omitted for clarity. Selected bond distances (Å): Pd1−C1 2.166(6), Pd1−C2 2.234(6), Pd1−C10 2.045(6), Pd1−N12 2.191(5), Pd1−N18 2.090(5).

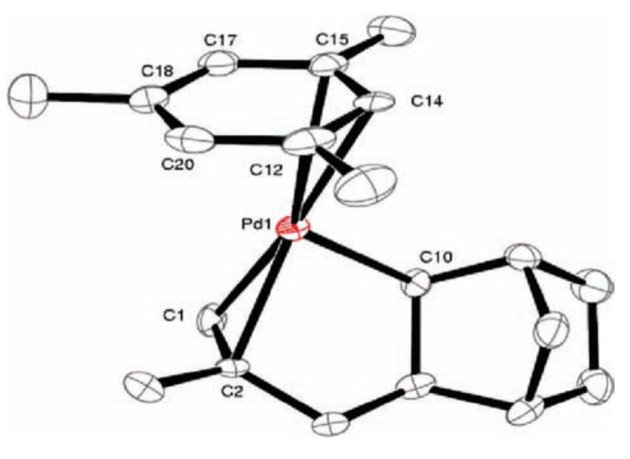
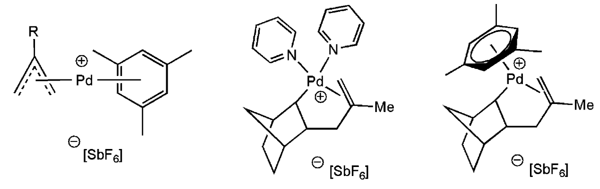


Figure 3. ORTEP diagram of the first insertion product **5-Me** (50% probability ellipsoids). Hydrogen atoms and the $[SbF_6]^-$ anion have been omitted for clarity. Selected bond distances (Å): Pd1−C1 2.145(6), Pd1−C2 2.180(5), Pd1−C10 2.063(5), Pd1−C12 2.450(6), Pd1−C14 2.331(6), Pd1−C15 2.435(6), Pd1−C17 2.607(6), Pd1−C18 2.677(6), Pd1−C20 2.594(6).

Chart 1



2-R **4-Me** **5-Me**

R= Cl, CO_2Me

difference in polymerization activity using low-temperature NMR spectroscopy.

Mechanistic Studies. Insertion of NB into the Pd−Allyl Bond in (1-Me)$_2$. We have recently demonstrated that the coupling event between NB and the allyl fragment in [(2-Me-allyl)Ni(μ-Cl)]$_2$ is a reversible process which occurs at low temperatures. No intermediates were detected by NMR spectroscopy during the insertion and deinsertion process (Scheme 3a).[14] However, insertion for the Pd system **(1-Me)$_2$** occurs at higher temperatures compared to the analogous Ni system which might allow intermediates to be discerned by NMR spectroscopy.

When 2 equiv of NB were added to a CD_2Cl_2 solution of **(1-Me)$_2$** at −94 °C, vinylic resonances due to both free (δ 5.93) and bound (δ 5.26 and 5.14, $^3J_{HH} = 3.5$ Hz) NB are detected. All four allyl resonances in the NB π-adduct are inequivalent and resonate at δ 4.43, 4.35, 3.47, and 2.90 (Figure S1, Supporting Information). As the temperature is raised, these signals diminish and are nearly undetectable at −29 °C as the equilibrium shifts torward **(1-Me)$_2$** and NB at higher temperatures. Broadening of the NB resonance at −20 °C suggests rapid exchange between NB and the minor amount of **1-Me(NB)** present. Above −20 °C only resonances due to **(1-Me)$_2$** and free NB are observed (Figure S2a, Supporting Information). However, at room temperature and above, resonances corresponding to the insertion product **(3-Me)$_2$** start to appear (Scheme 3b, also see Figure S2b in the Supporting Information).[17] The exchange between free and bound NB to form **1-Me(NB)** was confirmed by NOESY NMR techniques at low temperatures (−92 °C). The free energy for this equilibrium process has been evaluated to be ΔG (−92 °C) = −1.7 kcal mol^{-1} (see Supporting Information for details, Figure S3).

Reactivity of 4-Me with B(C$_6$F$_5$)$_3$ and the Generation of the Active Catalyst Species. We have recently used [(2-R-allyl)Ni(NCMe)$_2$][B(Ar$_F$)$_4$] (R = H or Me and $[B(Ar_F)_4]^- = [B(C_6H_3(CF_3)_2)_4]^-$, as a precursor to generate "ligand-free" complexes of the type [(2-R-allyl)Ni$^+$(Ar$_F$)B$^-$(Ar$_F$)$_3$] on addition of a Lewis acid, $B(C_6F_5)_3$. In these complexes one of the aryl rings of the $[B(Ar_F)_4]^-$ ligand is weakly coordinated to the cationic Ni(II) center and it is readily displaced to generate highly active catalysts for the polymerization of 1,3-dienes such as butadiene and isoprene and NB to yield highly cis enchained polymer[18] and high-molecular-weight poly(norbornene), respectively.[14]

No polymerization activity is observed for **4-Me** in the absence of $B(C_6F_5)_3$ similar to [(2-R-allyl)Ni(NCMe)$_2$][B(Ar$_F$)$_4$]. However, on addition of $B(C_6F_5)_3$ the activated complex polymerizes NB at 23 °C with 150 TOs within 1 h. Although the polymer samples exhibited narrow MWDs of about 1.4, no molecular weight control was achieved (Table 4).

In an attempt elucidate the identity of the active species in the vinyl addition polymerization of NB, NMR studies were undertaken. Colorless CD_2Cl_2 solutions of **4-Me** immediately undergo a color change to yellow on addition of $B(C_6F_5)_3$ (4 equiv) and the ^{19}F NMR spectrum shows resonances attributable to the py•B(C$_6$F$_5$)$_3$ adduct (δ −131.9, −157.4, −164.0), free borane (δ −127.2, −142.9, −160.4), and a third species that shows resonances at δ −139.2 (d, $^3J_{FF} = 19$ Hz), −154.5 (t, $^3J_{FF} = 21$ Hz), and −162.7 (dd, $^3J_{FF} = 19$ and 21 Hz). The ^{19}F NMR chemical shifts of the py•B(C$_6$F$_5$)$_3$ adduct are in good agreement with the ones reported for the DMAP•B(C$_6$F$_5$)$_3$ adduct of δ −131.7, −157.6, and −163.5.[19] The last set of resonances at δ −139.1, −154.5, and −162.7 may be attributed to a py•B(C$_6$F$_5$)$_3$ adduct which coordinates to the cationic [(2-Me-propenyl-norbornyl)Pd]$^+$ species in analogy to [(2-R-allyl)Ni$^+$(Ar$_F$)B$^-$(Ar$_F$)$_3$] (Scheme 4). The precise coordination mode of this adduct to the cationic Pd center is hard to elucidate with certainty, and it might occur via the π-system of either the pyridine ring or of a fluorinated aryl ring of the borane. However, coordination to the π-system of the pyridine moiety seems to be the most reasonable assumption consistent with the NMR spectroscopic results. On cooling of the reaction mixture in the NMR probe in an attempt to freeze out any fluctionality, precipitation occurred most likely due to the low solubility of the pyridine-derived $B(C_6F_5)_3$ adducts[19] which makes low-temperature NMR studies to either elucidate dynamics or the reactivity toward NB very challenging. Regardless of the nature of the coordination, the pyridine-borane adduct serves as a capping ligand for the cationic [(2-Me-propenyl-norbornyl)Pd]$^+$ species similar to [(2-R-allyl)Ni$^+$(Ar$_F$)B$^-$(Ar$_F$)$_3$] and therefore activating complex **4-Me** for the polymerization. Since the catalytic activity of **4-Me/**B(C$_6$F$_5$)$_3$ is similar to **5-Me** but requires the addition of cocatalyst, the reactivity of **5-Me** toward NB will be considered in the following section.

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(17) The interaction of **(1-Cl)$_2$** toward NB was also investigated, and the results are similar to (**1-Me)$_2$** (see Experimental Section for details). However, on the experimental scale the reaction did not proceed in benzene at 50 °C, and in refluxing CH_2Cl_2 only incomplete conversion was achieved. Furthermore, prolonged heating did not improve the conversion; instead polymer and palladium metal formation was observed.

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Table 1. Polymerization of NB with [(2-Cl-allyl)Pd(mesitylene)][SbF$_6$] **(2-Cl)**[a]

entry	time (min)	temp (°C)	cat (mmol)	NB/Ni mol ratio	% conversion[b]	M_n[b]	M_w[b]	MWD[b]	TON[b]
1	2	0	2.0×10^{-5}	234	2	77 600	99 200	1.3	5
2	5	0	2.0×10^{-5}	234	10	112 000	153 000	1.4	23
3	10	0	2.0×10^{-5}	234	58	184 100	240 000	1.3	136
4	15	0	2.0×10^{-5}	234	79	231 000	310 000	1.3	185
5	20	0	2.0×10^{-5}	234	87	215 300	297 100	1.4	204
6	25	0	2.0×10^{-5}	234	100	255 100	316 600	1.2	234
7	5	23	2.0×10^{-5}	467	100	165 700	202 000	1.1	467

[a] TON, (moles monomer)(conversion)/moles catalyst. Polymerization conditions: 10 mL total volume, CH_2Cl_2 (2 mL); methylcyclohexane (7 mL), NB stock solution (4.67 M) in methylcyclohexane (1 mL). [b] Averaged over several trials.

Table 2. Polymerization of NB with [(2-CO$_2$Me-allyl)Pd(mesitylene)][SbF$_6$] **(2-CO$_2$Me)**[a]

entry	time (min)	temp (°C)	cat (mmol)	NB/Ni mol ratio	% conversion	M_n	M_w	MWD	TON
1	10	0	2.0×10^{-5}	234	3	126 200	176 500	1.4	7
2	20	0	2.0×10^{-5}	234	27	232 000	300 000	1.3	63
3	25	0	2.0×10^{-5}	234	69	273 000	357 000	1.3	161
4	30	0	2.0×10^{-5}	234	71	295 000	367 800	1.3	166
5	40	0	2.0×10^{-5}	234	94	274 700	370 000	1.4	220
6	50	0	2.0×10^{-5}	234	96	288 400	393 800	1.4	225
7[b]	50	0	2.0×10^{-5}	234	90	103 400	135 600	1.3	211

[a] TON, (moles monomer)(conversion)/moles catalyst. Polymerization conditions: 10 mL total volume, CH_2Cl_2 (2 mL), methylcyclohexane (7 mL), NB stock solution (4.67 M) in methylcyclohexane (1 mL). [b] Addition of $B(C_6F_5)_3$ (2 equiv) before NB addition.

Table 3. Polymerization of NB with [(2-Me-propenylnorbornyl)Pd(py)$_2$][SbF$_6$] **(4-Me)**/B(C$_6$F$_5$)$_3$[a]

entry	time (min)	temp (°C)	cat (mmol)	NB/Ni mol ratio	% conversion	M_n[b]	M_w[b]	MWD[b]	TON[b]
1	15	23	1.68×10^{-5}	150	8	86 000	123 000	1.4	12
2	30	23	1.68×10^{-5}	150	35	106 000	150 000	1.4	53
3	45	23	1.68×10^{-5}	150	75	155 000	206 000	1.3	113
4	60	23	1.68×10^{-5}	150	98	209 000	263 000	1.3	147

[a] TON, (moles monomer)(conversion)/moles catalyst. Polymerization conditions: 10 mL total volume, CH_2Cl_2 (2 mL), methylcyclohexane (6 mL), NB stock solution (1.26 M) in methylcyclohexane (2 mL). [b] Averaged over several trials.

Table 4. Polymerization of NB with [(2-Me-propenylnorbornyl)Pd(mesitylene)][SbF$_6$] **(5-Me)**[a]

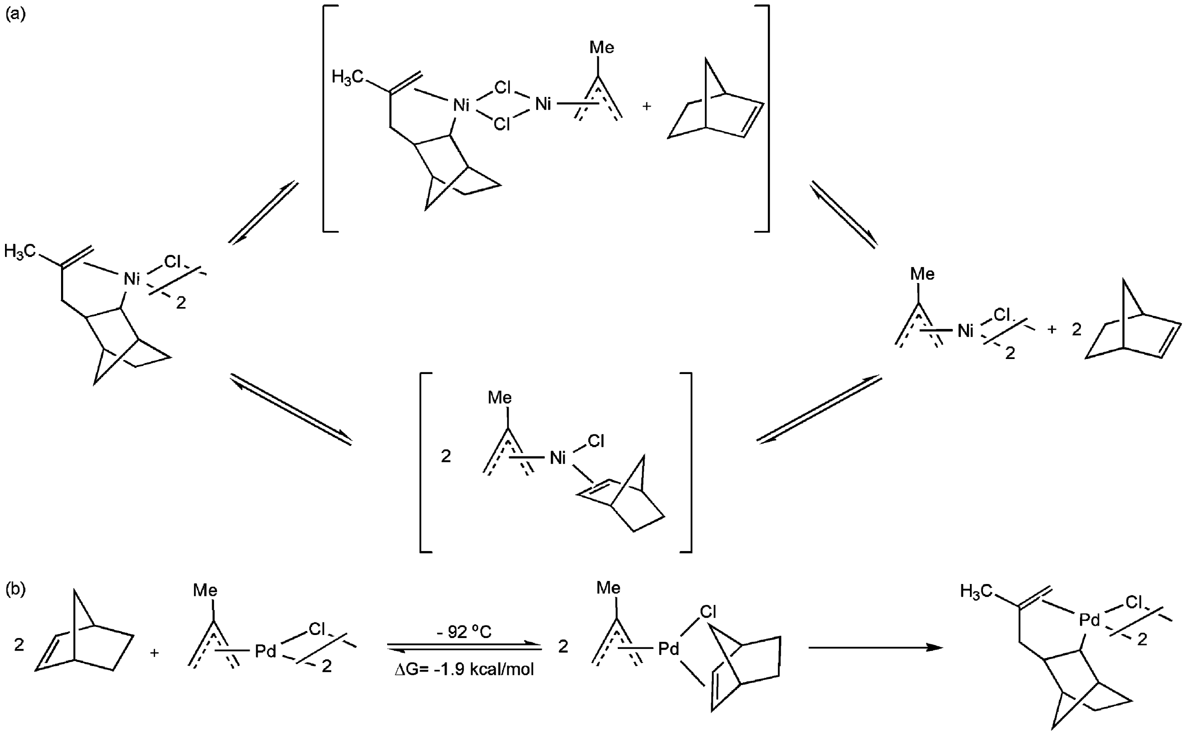
entry	time (min)	temp (°C)	cat (mol)	NB/Ni mol ratio	% conversion	M_n[b]	M_w[b]	MWD[b]	TON[b]
1	2	23	1.6×10^{-5}	200	3	n/d	n/d	n/d	6
2	5	23	1.6×10^{-5}	200	10	380 000	460 000	1.2	20
3	7	23	1.6×10^{-5}	200	18	430 000	496 000	1.2	36
4	10	23	1.6×10^{-5}	200	30	466 000	560 000	1.2	60
5	15	23	1.6×10^{-5}	200	37	526 000	660 000	1.3	74
6	20	23	1.6×10^{-5}	200	41	564 000	723 000	1.3	82
7	30	23	1.6×10^{-5}	200	48	616 000	791 000	1.3	96
8	45	23	1.6×10^{-5}	200	85	656 000	907 000	1.4	170
9	60	23	1.6×10^{-5}	200	100	663 000	917 000	1.4	200

[a] TON, (moles monomer)(conversion)/moles catalyst. Polymerization conditions: 10 mL total volume, CH_2Cl_2 (2 mL), methylcyclohexane (6 mL), NB stock solution (1.60 M) in methylcyclohexane (2 mL). [b] Averaged over several trials.

Reactivity of 2-Me and 5-Me toward NB. Addition of 1 equiv of NB at −120 °C to a $CDCl_2F$ solution of **2-Me** immediately forms the first insertion product **5-Me**, and the chemical shifts agree with independently synthesized **5-Me** (Figure S4 in Supporting Information). This observation indicates that the first insertion is not rate-determining under polymerization conditions and thus **2-Me** and **5-Me** will exhibit similar catalytic activities. Addition of another equivalent of NB to this reaction mixture or to solutions of isolated **5-Me** leads to instantaneous displacement of mesitylene to yield **7-Me** (Scheme 5). This behavior is consistent with our reactivity studies on **2-Me** in which the mesitylene ligand is rapidly displaced by olefins and alkynes to form bis(olefin) and bis(alkyne) adducts, respectively.[13] However, **5-Me** behaves differently relative to the analogous Ni species for which the mesitylene exchange is too slow to be observed on the NMR time scale.[14] Furthermore, the NMR data obtained for 7-**Me** are inconsistent with a 2:1 adduct such as [(2-Me-propenylnorbornyl)Pd(π-norbornene)$_2$]$^+$ species which might be expected based on our studies of the reactions of olefins and alkynes with **2-Me**[13] but are more consistent with a 1:1 adduct. The addition of two equivalents of NB relative to Pd induces a rapid exchange between free and bound NB that cannot be completely frozen out at temperatures as low as −140 °C, and the formation of a 2:1 adduct cannot be observed.

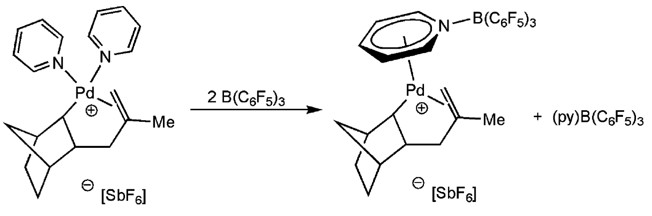
The best resolved spectra of **7-Me** were obtained when only ca. 0.9 equiv of NB was added to **5-Me** at −120 °C (Figure S5, Supporting Information). Various 1D and 2D NMR techniques were employed to gain structural information on **7-Me**. The vinyl protons of the coordinated NB are inequivalent and resonate at δ 6.19 and 5.81. However, the most notable feature in the resulting ^{1}H NMR spectrum of **7-Me** is a high-field doublet at δ −1.28 ($^2J_{HH}$= 11.5 Hz) of intensity 1 which correlates in the ^{1}H−^{1}H COSY NMR spectrum to a doublet at δ 1.52 ($^2J_{HH}$= 11.5 Hz), also of intensity 1 (Figure S6, Supporting Information). Additionally, both protons are attached to the same carbon atom resonating at δ 42.5 as confirmed by

Scheme 3



(1-Me)$_2$ **1-Me(NB)** **(3-Me)$_2$**

Scheme 4



4-Me **6-Me**

a ^{1}H−^{13}C HSQC NMR experiment (Figure S7a and S7b, Supporting Information). These spectroscopic data support the formulation of **7-Me** as a species in which one NB molecule binds via the π-system and a γ-agostic interaction to the syn hydrogen atom at C7. *Therefore, NB can act as a bidentate ligand* (Scheme 6). This interaction is further supported by the $^1J_{\mathrm{CH}}$ coupling constants for the agostic and nonagostic hydrogen atom attached to C7 of 110 and 160 Hz, respectively (Figure S8, Supporting Information).[20,21]

However, the final piece of evidence came from a crystal structure analysis of **7-Me** isolated from the NMR sample of **5-Me** and NB (~0.9 equiv) in $CDCl_2F$. For this purpose, the yellow $CDCl_2F$ solution was layered with pentane and kept at −80 °C for 3 days to yield light yellow crystals of **7-Me** (Figure 4).

The structural motif of a NB molecule acting as a bidentate ligand binding via the olefin funtionality and an agostic interaction to the methylene bridge is rare, but has been observed in a neutral trinuclear Ru cluster,[22] [(nacnac)Rh(norbornene)] (nacnac = (2,6-$Me_2C_6H_3$)NC(Me)CHC(Me)N($C_6H_3Me_2$-2,6))[23] and a cationic [(dien)Cu(norbornene)]$^+$ (dien = HN($CH_2CH_2NH_2$)$_2$) complex.[24] The constrained bicyclic structure of NB aligns C15−H15b nearly perfectly to fill the fourth coordination site around the square-planar cationic Pd center leading to a short Pd1−C15 distance of 2.756(6) Å and a Pd1−H15b distance[25] of 2.186(73) Å.

The observation of **7-Me** as an intermediate in the NB polymerization process is significant since a similar agostic interaction has been invoked to explain the 2-exo,7′-syn linkage in NB oligomers generated by a cationic zirconocene catalyst,[6] and it also suggests an important structural motif with respect to the catalytically active species during polymerization. Although we were unable to detect other intermediates in the polymerization process by NMR spectroscopy, we suggest that the bidentate coordination mode of NB and/or an agostic interaction involving the growing polymer chain also prevail in the propagating species. This contradicts Goodall's proposed active site in which the "naked" Ni(II)/Pd(II) species is believed to contain only the growing polymer chain and two NB monomers bound exclusively via the π-system to form an unlikely 14 valence electron intermediate.[1]

5-Me and NB (ratio ≈ 1:1.1) were mixed at −140 °C followed by warming and monitoring **7-Me** by NMR: At −130 °C, the exchange between bound and the small fraction of free NB is nearly frozen out and the vinylic resonances of the bound NB, as well as its agostic CH resonance, are observed at the

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(20) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395–408.

(21) Brookhart, M.; Green, M. L. H.; Parkin, G. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 6908–6914.

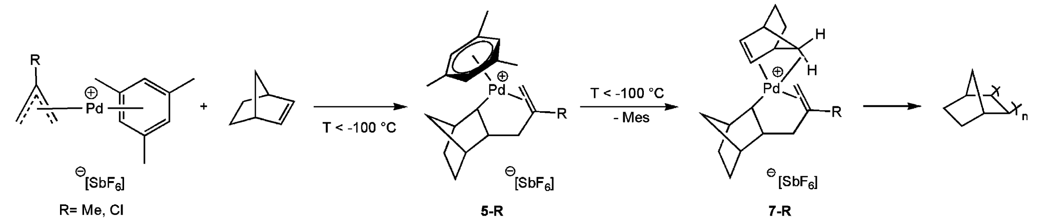
(22) Brown, D. B.; Cripps, M.; Johnson, B. F. G.; Martin, C. M.; Braga, D.; Grepioni, F. *Chem. Comm.* **1996**, 1426–1427.

(23) Budzelaar, P. H. M.; Moonen, N. N. P.; de Gelder, R.; Smits, J. M. M.; Gal, A. W. *Eur. J. Inorg. Chem.* **2000**, 753–769.

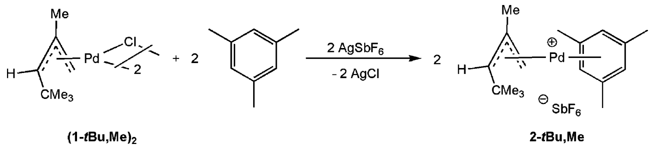
(24) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A.; Chiesi-Villa, A. *J. Am. Chem. Soc.* **1978**, *100*, 4918–4919.

(25) The "X-ray determined" bond length is a measure of the distance between the centroids of the electron density of the two atoms concerned, and the centroid of the electron density around a covalently bonded hydrogen atom is not coincident with its nuclear position but is displaced significantly in the direction of the hydrogen−(other atom) σ-bond. (Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213–1214.)

Scheme 5



Scheme 6



same positions as described above when a 1:0.9 ratio was used. On warming, the two vinylic resonances of the bound NB begin to broaden, reach coalescence at −86 °C, and then sharpen with increasing temperature to a single resonance. Loss of NB from Pd renders the vinylic hydrogens equivalent, and thus, the coalesced signal represents the weighted average of the two bound vinyl signals and the vinyl signals of the small fraction of free NB present. Loss of NB from **7-Me** and recoordination will result in site exchange of the agostic $CH_{7\text{-syn}}$ proton of **7-Me** with the $H_{7\text{-syn}}$ proton of free NB (present in very low concentration relative to **7-Me**). This exchange process results in the δ −1.28 resonance of **7-Me** at −120 °C (slow exchange) moving downfield to δ −0.65 at −12 °C (weighted average resonance of agostic $H_{7\text{-syn}}$ of **7-Me** plus $H_{7\text{-syn}}$ of free NB) (see Supporting Information, Figure S9 for details). Addition of variable concentrations of NB suggests that this exchange process is associative in nature. Further evidence for this assumption is provided when a more bulky substituted allyl ligand is used (see below).

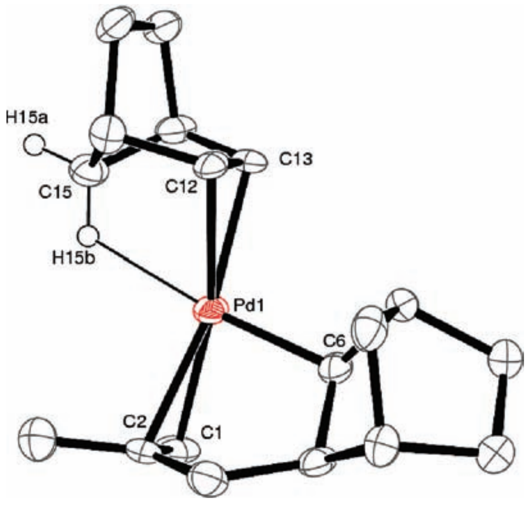


Figure 4. ORTEP diagram of the agostic complex **7-Me** (50% probability ellipsoids). All hydrogen atoms were located in the difference Fourier map. Hydrogen atoms were included in calculated positions using a riding model, but not refined, except the geminal hydrogen atoms on C15, which have been refined isotropically. The hydrogen atoms and the $[SbF_6]^-$ anion have been omitted for clarity, except the ones attached to C15. Selected bond distances (Å): Pd1−C1 2.218(6), Pd1−C2 2.286(6), Pd1−C6 2.042(6), Pd1−C12 2.257(6), Pd1−C13 2.236(6), Pd1−C15 2.756(6), Pd1−H15b 2.186(73).

As mentioned above, coordinated NB in **7-Me** exchanges rapidly on the NMR time scale. In the presence of a significant excess of free NB, the exchange is fast even at temperatures as low as −150 °C, and on warming, rapid polymer formation is observed above −20 °C. While no additional intermediates can be detected by NMR spectroscopy, free mesitylene never competes with free NB as a ligand for the cationic Pd center. These observations are consistent with a slow second insertion, viz., the opening of the olefin-chelate is rate-determining, relative to chain propagation.

On the basis of these studies, we reasoned if indeed chelate opening is the rate-determining step dictating slow insertion of a second NB monomer, the introduction of electron-withdrawing or sterically demanding groups into the allyl fragment should destabilize the chelate. The hypothesis regarding the influence of electron-withdrawing groups on the polymerization process is indirectly supported by the bulk polymerization results described for catalysts **2-Cl** and **2-CO$_2$Me** which are both significantly more active than **5-Me** and **4-Me**/B(C_6F_5)$_3$ (Tables 1−4). However, the decrease in reactivity moving from **2-Cl** to **2-CO$_2$Me** remains unexplained and appears to be counterintuitive: The ester functionality is a stronger electron-withdrawing group than chloride, and therefore, an increased reactivity might be expected.[26] To address this discrepancy we investigated the interaction of **2-Cl** and **2-CO$_2$Me** with NB by low-temperature NMR experiments.

Influence of Electron-Withdrawing Groups on the Allyl Fragment (R = Cl and CO$_2$Me). The bulk polymerization experiments described above clearly showed that the NB polymerization initiated by **2-Cl** exhibited the highest reactivity within the group of catalysts investigated. Therefore, 1 equiv of NB was added to a $CDCl_2F$ solution of **2-Cl** below −120 °C, and monitored by NMR spectroscopy. The insertion into the allyl−Pd bond was instantaneous and **5-Cl** formed immediately under these conditions (Scheme 6). Details regarding the NMR characterization are described in the Experimental Section. On further addition of ca. 1 equiv of NB to **5-Cl**, the agostic intermediate **7-Cl** was formed quantitatively and identified by NMR spectroscopy. However, in the presence of a slight excess of NB in solution, the exchange process of free and bound NB is more rapid than in **7-Me**. Consequently, an NMR spectrum in which the NB exchange is completely frozen out on the NMR time scale is difficult to obtain even at temperatures as low as −140 °C. Therefore, **7-Cl** was generated on addition of only 1.6 equiv of NB to **2-Cl**. This lead to a 3:4 mixture of **5-Cl** and **7-Cl**, but the line shapes were sharp and allowed the complete characterization of **7-Cl** at −120 °C using a variety of 1D and 2D NMR techniques (see Experimental Section for details). The most noteworthy feature is the high field resonance in the ^1H NMR spectrum at δ −0.94 ($^2J_{HH}$ = 11.5 Hz)

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[26] March, J. *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*; 2nd ed.; McGraw-Hill: New York, 1977.

corresponding to the agostic C_7-H_{syn} proton, while the nonagostic C_7-H_{anti} proton resonates at δ 1.65 ($^2J_{HH} = 11.5$ Hz). An $^1H-^{13}C$ HSQC NMR experiment verified that both protons are attached to the same carbon (C_7) resonating at δ 43.2. However, the chemical shift separation between these protons of $\Delta\delta = 2.59$ is less than for the analogous **7-Me** complex ($\Delta\delta = 2.80$). There is also considerably less difference in the agostic and nonagostic $^1J_{CH}$ coupling constants in **7-Cl** (126 and 146 Hz) versus **7-Me** (110 and 160 Hz). These observations point toward a weaker agostic interaction for **7-Cl** as compared to **7-Me**. Note that for **7-Cl**, polymerization of NB occurs even at −120 °C over the course of several hours, while poly(norbornene) is rapidly formed above −40 °C, but no additional intermediates are detected. All these results are consistent with the observed increased reactivity of **2-Cl** during bulk polymerizations and with a slow initiation followed by rapid propagation. They also confirm that the second insertion of NB into **7-Cl** is rate-limiting; however, once this insertion occurs, all further insertions are rapid, consistent with our proposal of a rate-limiting chelate opening.

The decreased activity of **2-CO$_2$Me** is inconsistent with this proposal, since the electron-withdrawing ester functionality should allow for a weaker coordination of the olefin arm to the cationic Pd center and therefore a more facile chelate opening. Low-temperature NMR studies were undertaken to investigate this discrepancy. The reactivity of **2-CO$_2$Me** toward NB was rather surprising. In contrast to **2/5-Me** and **2/5-Cl** displacement of coordinated mesitylene is considerably slower for **2/5-CO$_2$Me**. For example, treatment of **2-CO$_2$Me** with 5 equiv of NB at −120 °C in $CDCl_2F$ results in formation of **5-CO$_2$Me** as a major species with minor amounts of **2-CO$_2$Me** remaining together with a small fraction of agostic complex **7-CO$_2$Me**.[27] (Under these conditions, **2-Me** or **2-Cl** would have been fully converted to **7-Me** or **7-Cl**). Warming to −98 °C results in disappearance of **2-CO$_2$Me** and NMR evidence shows that the bound NB of **7-CO$_2$Me** is in rapid exchange with free NB. Further warming to −64 °C results in formation of poly(norbornene) with **5-CO$_2$Me** as the sole observable Pd species in solution. Signals for free mesitylene and bound mesitylene in **5-CO$_2$Me** are sharp at −64 °C indicating slow exchange on the NMR time scale. These results indicate again that chelate opening in the agostic intermediate (**7-CO$_2$Me**) is slow relative to propagation, but that a further barrier to initiation is formation of **7-CO$_2$Me** from **5-CO$_2$Me**. This added barrier likely explains the unexpected rate order **2-Cl** > **2-CO$_2$Me**.

We also investigated the possibility of activating the ester functionality on addition of $B(C_6F_5)_3$ to **2-CO$_2$Me**. To this end **2-CO$_2$Me** and $B(C_6F_5)_3$ (1.5 equiv) were dissolved in $CDCl_2F$. The resonances of **2-CO$_2$Me/B(C$_6$F$_5$)$_3$** broadened at low temperature significantly compared to **2-CO$_2$Me**, but at −130 °C the solubility of the resulting adduct is very low and it precipitated from solution. However, relatively sharp resonances were observed at −110 °C. In the $^{13}C\{^1H\}$ NMR spectrum, both resonances of the ester functionality, CO_2Me, shift on exposure to $B(C_6F_5)_3$ downfield by ca. 2 ppm (see Experimental Section for details) consistent with an interaction of the ester functionality with the electron-deficient borane,[28] while the remaining resonances are nearly unchanged, although broadened. NB was added to this activated complex **2-CO$_2$Me/B(C$_6$F$_5$)$_3$** and the observations for this system are qualitatively similar to unactivated **2-CO$_2$Me**. After warming of the reaction mixture to −64 °C in the NMR probe **2-CO$_2$Me/B(C$_6$F$_5$)$_3$)** converted to **5-CO$_2$Me/B(C$_6$F$_5$)$_3$** as the only Pd-containing species detectable in solution and insoluble poly(norbornene).

In summary, installing electron-withdrawing groups in the 2-position of the allyl fragment indeed facilitates chelate opening in the agostic intermediate **7-R** as initially hypothesized. However, very electron-withdrawing groups such as $-CO_2Me$ or borane-coordinated $-CO_2Me$ render the cationic Pd center so electron-poor that the rate of mesitylene displacement becomes slow and provides an additional barrier to insertion. This feature demonstrates a significant drawback of this catalyst architecture with respect to achieving living polymerization.

Influence of a Sterically Demanding Substituent in the 1-Position of the Allyl Fragment (R = *t*Bu, Me). Another possible solution to influence chelate opening is to introduce steric strain into the allyl moiety. For this purpose the dimer **(1-*t*Bu,Me)$_2$** was synthesized which bears a bulky *tert*-butyl substituent in the 1-anti position.[29−31] This 1-anti *tert*-butyl group is expected to disfavor the π-coordination in the **5-*t*Bu,Me** and **7-*t*Bu,Me** intermediates.

The synthesis of **2-*t*Bu,Me** is straightforward and follows the procedures as described for other **2-R** (R = Me, Cl and CO_2Me) systems (Scheme 6, see Experimental Section for details). Although no bulk polymerizations were undertaken with this catalyst system, the reactivity of **2-*t*Bu,Me** toward NB was studied using low-temperature NMR spectroscopy. The results of this study were rather surprising: On addition of 3 equiv of NB to a $CDCl_2F$ solution of **2-*t*Bu,Me** at −86 °C complete displacement of mesitylene was observed (Scheme 7). However, in contrast to **2-Me**, the first insertion of NB into the Pd−allyl bond was not instantaneous as anticipated. This is substantiated by the following observations: (a) on addition of NB three high-field resonances (which are strongly coupled to the low-field resonances given in parentheses) at δ −0.94 (1.44), −0.30 (0.63), and −0.05 (0.76) were observed, suggesting the presence of three distinct species containing an agostic interaction between the *syn*-H_7 of NB and the cationic Pd center, (b) two of these species (δ −0.30 and −0.05) convert over time or on further addition of NB into **7-*t*Bu,Me** which is an analogue species to **7-R** (R = Me, Cl) as substantiated by NMR spectroscopy and single-crystal X-ray diffraction (Figure 5), (c) the integration of the diastereoptopic CH_2 resonances (δ 2.64−2.59) which are uniquely indicative for a first insertion product correlate to the highest field agostic resonance (δ −0.94) corresponding to the **7-*t*Bu,Me** species, and (d) no further intermediates were observed on warming the NMR sample to −40 °C, but slow polymer formation occurred. Note the coupling of NB occurs exclusively to C_3, the less-substituted carbon of the π-allyl moiety. This behavior agrees with the observations concerning [(1-Me-allyl)Pd(COD)][PF_6][1] but contrasts to [(1-Me-allyl)Ni(mesitylene)][$B(Ar_F)_4$] in which NB couples to the more-substituted allylic carbon.[14]

These data strongly suggested that the two other agostic species observed at δ −0.30 and −0.05 are attributable to prefirst insertion complexes. Hence, it was of interest to characterize the identity of these preinsertion products in more detail. To this end, 0.6 equiv of NB was added to a frozen $CDCl_2F$ solution

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[27] This sample of **2-CO$_2$Me** contained ca. 1 equiv of mesitylene which may influence the ratio of **5-CO$_2$Me/7-CO$_2$Me**.

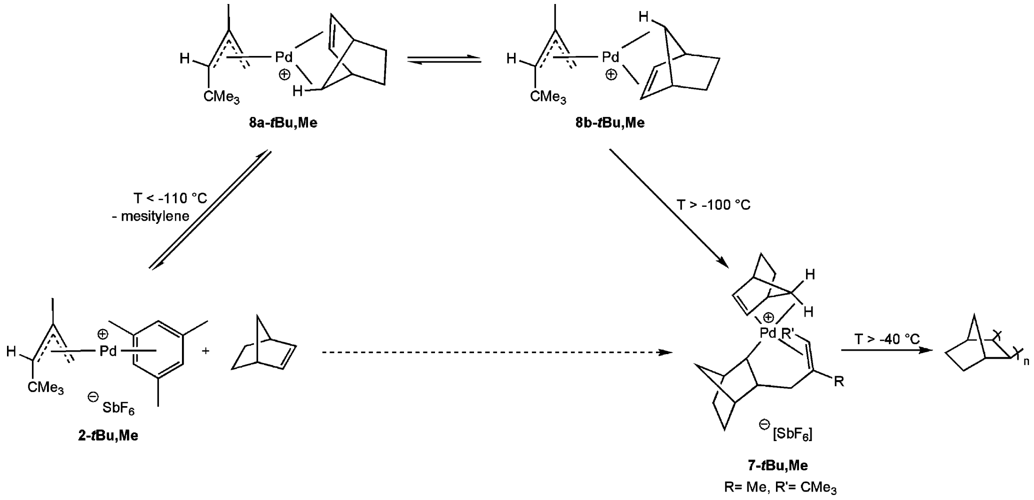
[28] Parks, D. J.; Piers, W. E.; Parvez, M.; Atencio, R.; Zaworotko, M. J. *Organometallics* **1998**, *17*, 1369–1377.

[29] Lukas, J.; Ramakers-Blom, J. E.; Hewitt, T. G.; De Boer, J. J. *J. Organomet. Chem.* **1972**, *46*, 167–177.

[30] Volger, H. C. *Rec. Trav. Chim.* **1968**, *87*, 225–240.

[31] Lukas, J.; Coren, S.; Blom, J. E. *Chem. Comm.* **1969**, 1303–1304.

Scheme 7



of **2-*t*Bu,Me**, mixed at −140 °C, and inserted into a precooled NMR probe (−120 °C). Under these conditions 40% of unreacted **2-*t*Bu,Me** remained in solution (as expected), while the two preinsertion species, **8a-*t*Bu,Me** and **8b-*t*Bu,Me**, were formed in a ca. 1:1 ratio (>50%) and **7-*t*Bu,Me** was formed in less than 10% (Scheme 7). Attention to detail must to be observed, otherwise **7-*t*Bu,Me** is readily formed in significant quantity at the expense of **8a-*t*Bu,Me** and **8b-*t*Bu,Me**. Interestingly, even at −130 °C the two preinsertion species exchange with each other as substantiated by a significant line-broadening relative to the line shapes for **2-*t*Bu,Me** at the same temperature ($\upsilon_{1/2}$ = 8 vs 4 Hz). (We note that the chemical shifts of the preinsertion complexes at δ −0.19 (0.90) and 0.22 (0.77) (low-field resonances are given in parentheses), respectively, are slightly different at this temperature and solvent compared to CD_2Cl_2 at −86 °C.) The $^1J_{CH}$ coupling constants of the agostic and nonagostic H_7 resonances in both species are only slightly different, 135 vs 138 Hz and 131 vs 139 Hz, respectively, indicating only a very weak agostic interaction in both species and also explaining the facile exchange of NB between these species at this temperature.

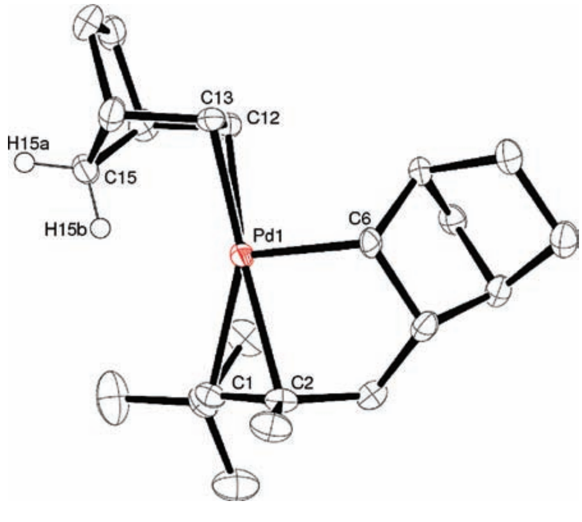


Figure 5. ORTEP diagram of the agostic complex 7-***t*Bu,Me** (50% probability ellipsoids). All hydrogen atoms were located in the in the difference Fourier map. Hydrogen atoms were included in calculated positions using a riding model but not refined, except the geminal hydrogen atoms on C15, which have been refined isotropically. The hydrogen atoms and the $[SbF_6]^-$ anion have been omitted for clarity, except the ones attached to C15. Selected bond distances: Pd1−C1 2.330(4), Pd1−C2 2.326(4), Pd1−C6 2.084(3), Pd1−C12 2.237(4), Pd1−C13 2.194(4), Pd1−C15 2.852(4), Pd1−H15b 2.33(5).

There are a few notable features in the crystal structure of **7-*t*Bu,Me** compared to **7-Me**. The Pd1−C1, Pd1−C15, and Pd1−H15b distances are significantly elongated by ca. 0.12 Å which reflects the steric bulk introduced by the 1-*tert*-butyl group.[25] The weakening of the agostic interaction is also reflected by the reduced chemical shift separation between the agostic and nonagostic protons of $\Delta\delta$ = 2.38. Despite the weakened agostic interaction, the exchange between free and bound NB is slow on the NMR time scale. However, this discrepancy is readily explained when considering a space-filling model of **7-*t*Bu,Me**, which shows that the Pd center is effectively shielded by the bulky *tert*-butyl group, and therefore, the rate of intermolecular associative exchange between free and bound NB is slow.

In conclusion, the problem of slow initiation cannot to be resolved by introducing a bulky group in close proximity to the metal, since the first insertion step becomes rate-limiting together with a still slow opening of the π-coordinate chelate arm.

Conclusions

Several cationic (allyl)Pd(II) complexes have been studied for the (2,3)-vinyl addition polymerization of NB which exhibit good to high activity. For example the most active catalyst, **2-Cl** produces 470 TOs in less than 5 min at 23 °C while only 200 TOs are achieved within 1 h at 23 °C for **5-Me** (Tables 1 and 3). In all cases the NMR and polymerization data point to a slow initiation process coupled with a rapid propagation rate for polymerization which prevents living polymerization and therefore polymer molecular weight control. In this context the remarkably narrow MWD values of 1.2−1.4 might appear counterintuitive, but Gold has shown using statistical analyses that such MWD values are completely consistent with a very slow initiation event followed by very rapid propagation.[32]

The high polymerization rates and the fact that only a small fraction of the Pd species is responsible for polymer formation imply that the barrier to NB insertion in these propagating species must be extremely low. However, the first-formed intermediate in polymerizations initiated with [(2-R-allyl)Pd-

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[32] Gold, L. *J. Chem. Phys.* **1958**, *28*, 91–99.

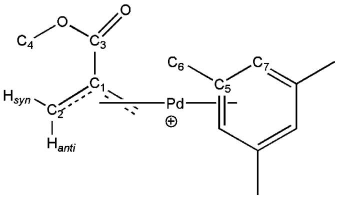
(mesitylene)]$^+$ complexes has been fully characterized (NMR and X-ray diffraction) and shown to be a species in which the allyl and NB units couple in a cis-exo fashion to yield a σ,π-complex capped by mesitylene, **5-R**. This coupling event is very fast and occurs at temperatures as low as −120 °C. In the presence of free NB the mesitylene ligand is readily displaced to form the agostic intermediate **7-R** which has also been fully characterized by various NMR techniques and in two cases **7-Me** and **7-*t*Bu,Me** by X-ray diffraction. The observation of this intermediate is significant since, to date, no group has achieved spectroscopic characterization of these propagating species that bear no ancillary ligands. The ability of NB to act as a bidentate ligand is most likely an important structural element for the stabilization of the propagating species which we, unfortunately, cannot observe by NMR. The fact that polymer formation occurs from the intermediate **7-R** in the presence of excess NB and no other intermediates are observed strongly argues for the second insertion, i.e., insertion of NB in **7-R**, being the slow initiation step and, that following the second insertion, propagation is extremely fast. This leads to the conclusion that chelate opening in **7-R** is the most severe restriction preventing a living polymerization in these systems. In principle, this limitation might be overcome by introducing electron-withdrawing or sterically demanding groups on the allyl fragment. While the reaction rate significantly increases for **2-Cl** due to a more rapid initiation (second insertion), a decrease is observed in the case of the more electron-withdrawing **2-CO$_2$Me** system. NMR studies show that in the **2/5-CO$_2$Me** system displacement of mesitylene is slow compared to the **2/5-Cl** system and provides a further barrier to initiation. The introduction of a sterically demanding t-butyl group in the 1-anti position allowed the observation of the γ-agostic preinsertion species **8a/b-*t*Bu,Me** in which the mesitylene ligand was displaced by one NB monomer. After NB has inserted into the less-substituted allyl carbon bond, mesitylene is readily displaced to form the γ-agostic species **7-*t*Bu,Me**. However, chelate opening continues to be the slow initiation step again preventing a living polymerization. In summary, in all systems investigated slow initiation relative to propagation was observed and could not be circumvented by altering the electronic and steric features of these allyl complexes. Currently we are investigating alternative systems which might overcome these restrictions and therefore ensure a living polymerization and control of polymer molecular weight.

Experimental Section

General Considerations. All reactions, unless otherwise stated, were conducted under an atmosphere of dry, oxygen-free argon using standard high-vacuum, Schlenk, or drybox techniques. Argon was purified by passage through BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves. All palladium catalysts were stored under argon in an MBraun glovebox at −35 °C. ^{1}H, ^{13}C{^{1}H}, ^{1}H−^{1}H COSY, ^{1}H−^{13}C HSQC, ^{1}H−^{1}H NOESY, ^{1}H−^{1}H TOCSY, and ^{13}C DEPT135 NMR spectra were recorded on a Bruker DRX 500 MHz, a Bruker DRX 400 MHz, or a Bruker 400 MHz AVANCE spectrometer. Chemical shifts are referenced relative to residual $CHCl_3$ (δ 7.24 for ^{1}H), $CH(D)Cl_2$ (δ 5.32 for ^{1}H), $CHCl_2F$ (δ 7.47 for ^{1}H), $^{13}CD_2Cl_2$ (δ 53.8 for ^{13}C), $^{13}CDCl_3$ (δ 77.0 for ^{13}C), and $^{13}CDCl_2F$ (δ 104.2 for ^{13}C). GPC analyses at high temperature were conducted in HPLC grade 1,2,4-trichlorobenzene at 140 °C using a Waters Alliance GPCV 2000 at the Cornell Center for Materials Research Polymer Characterization Facility. Molecular weights are reported relative to polystyrene standards. Thermal transitions were measured with a Seiko 220C DSC on the second heat with a heating rate of 10 °C min^{-1}. Elemental analyses were carried out by Robertson Microlit Laboratories of Madison, NJ. Structure factor tables are available from the authors upon request. Crystallographic data were also deposited with the Cambridge Crystallographic Data Centre. Copies of the data (CCDC No. 724661−724665) can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB 1EZ, U.K. (fax +44 1223 336033).

Materials. All solvents were deoxygenated and dried by passage over columns of activated alumina.[33,34] CD_2Cl_2, purchased from Cambridge Laboratories, Inc., was dried over CaH_2, vacuum-transferred to a Teflon sealable Schlenk flask containing 4 Å molecular sieves, and degassed via three freeze−pump−thaw cycles. Freon ($CDCl_2F$) was prepared according to a literature procedure and stored over activated 4 Å molecular sieves at −25 °C.[35] NB was purchased from Aldrich and dried by refluxing over activated 4 Å molecular sieves, followed by distillation.[36] $B(C_6F_5)_3$ was purchased from Strem and sublimed prior to use.[37] Mesitylene (1,3,5-$Me_3C_6H_3$) was purchased from Aldrich and used without further purification. $PdCl_2$ was purchased from J&J Materials and used as received. [(2-MeO$_2$C-allyl)PdCl]$_2$ **(1-CO$_2$Me)$_2$**, [(1-Me$_3$C-2-Me-allyl)Pd(μ-Cl)]$_2$ **(1-*t*Bu,Me)$_2$**, and [(2-R-allyl)Pd(Mesitylene)][SbF$_6$] **(2-R)** (R = H, Me, Cl), were synthesized according to literature methods.[13,29−31,38]

Synthesis.



2-CO$_2$Me

Synthesis of [(2-MeO$_2$C-allyl)Pd(mesitylene)][SbF$_6$] Complex (2-CO$_2$Me). Under an argon atmosphere, [(2-MeO$_2$C-allyl)PdCl]$_2$[38] (0.278 g, 0.578 mmol) was dissolved in dry methylene chloride (20 mL), and the resulting yellow solution was stirred at room temperature for 5 min to dissolve the solid. Excess mesitylene (0.50 mL, 3.57 mmol) was then added via syringe, and the resulting solution cooled in a dry ice/isopropanol bath to −78 °C. A solution of $AgSbF_6$ (0.397 g, 1.16 mmol) in 5 mL of methylene chloride was then added dropwise at −78 °C, and the mixture was stirred for ca. 30 min at this temperature before it was allowed to warm slowly to room temperature. The resulting yellow solution was cannula filtered and the solvent evaporated in vacuo. The product was washed with 3 × 10 mL of pentane and dried under vacuum to yield yellow powder, which was stored in the glovebox at −35 °C to prevent thermal degradation. Yield: 0.491 g. Low-temperature ^{1}H NMR analysis indicated the presence of free mesitylene; despite repeated attempts, free mesitylene could not be removed. ^{1}H NMR (500 MHz, CD_2Cl_2, −90 °C): δ 7.05 (s, 3H, mes-CH), 4.89 (s, 2H, H_{syn}), 3.75 (s, 3H, CH_3), 3.36 (s, 2H, H_{anti}), 2.40 (s, 9H, mes-CH$_3$). Free mesitylene (∼2 equiv) δ 6.92 (s, 6H, mes$_{Ar}$), 2.28 (s, 18H, mes$_{CH3}$). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, −90 °C): δ 162.9 (C_3), 132.1 (C_5), 115.1 (C_7), 107.6 (C_1), 64.8 (C_2), 53.7 (C_4), 20.2 (C_6). Free mesitylene (∼2 equiv) δ 140.2 (s, C_{ipso}), 123.0 (s,

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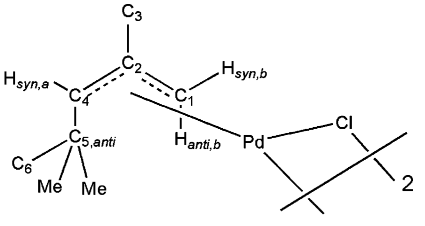
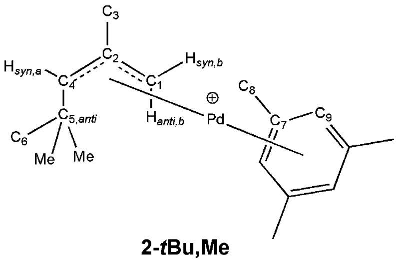
mesC$_{Ar}$), 20.9 (s, mes$_{CH3}$). ^{1}H NMR (500 MHz, CDCl$_2$F, −120 °C): δ 7.10 (s, 3H, mes-CH), 4.83 (s, 2H, H$_{syn}$), 3.80 (s, 3H, CH_3), 3.34 (s, 2H, H$_{anti}$), 2.40 (s, 9H, mes-CH$_3$). Free mesitylene (∼2 equiv) δ 6.97 (s, 6H, mes$_{Ar}$), 2.32 (s, 18H, mes$_{CH3}$). ^{13}C{^{1}H} NMR (125 MHz, CDCl$_2$F, −120 °C): δ 165.9 (C$_3$), 132.9 (C$_5$), 115.8 (C$_7$), 108.3 (C$_1$), 64.7 (C$_2$), 55.0 (C$_4$), 20.6 (C$_6$). Free mesitylene (∼2 equiv) δ 140.8 (s, C$_{ipso}$), 122.7 (s, mesC$_{Ar}$), 21.4 (s, mes$_{CH3}$).



(1-*t*Bu,Me)$_2$

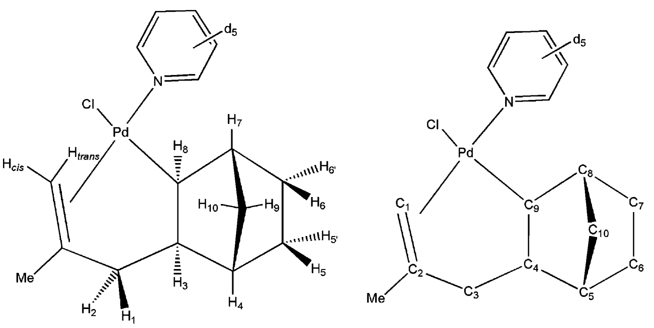
Synthesis of [(1-Me$_3$C-2-Me-allyl)Pd(μ-Cl)]$_2$ (1-tBu,Me)$_2$. (1-*t*Bu,Me)$_2$ was synthesized according to a literature procedure.[29−31] Repeated slow crystallization from MeOH at room temperature yielded **(1-*t*Bu,Me)$_2$** as the pure anti isomer. ^{1}H NMR (500 MHz, 20 °C, CDCl$_3$): δ 4.41 (s, 1H, H$_{syn,a}$), 3.81 (s, 1H, H$_{syn,b}$), 3.45 (s, 1H, H$_{anti,b}$), 2.01 (s, 3H, Me), 1.11 (s, 9H, CMe$_3$). ^{13}C{^{1}H} NMR (125 Hz, 293 K, CDCl$_3$): δ 118.3 (C$_2$), 92.5 (C$_4$), 62.1 (C$_1$), 36.7 (C$_5$), 31.3 (C$_6$), 26.3 (C$_3$).



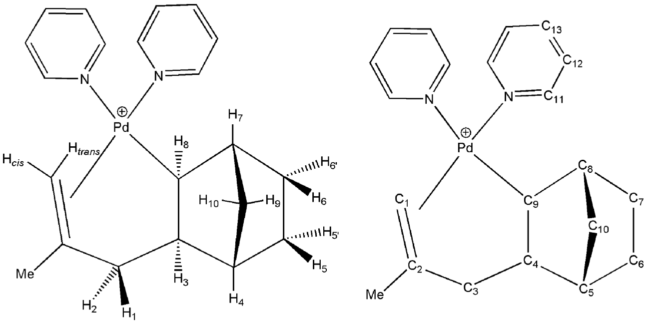
2-*t*Bu,Me

Synthesis of [(2-Me$_3$C-2-Me-allyl)Pd(mesitylene)][SbF$_6$] (2-tBu,Me). Under an argon atmosphere, a Schlenk flask was charged with **(1-*t*Bu,Me)$_2$** (0.341 g, 0.674 mmol) and AgSbF$_6$ (464 mg, mmol) and dissolved in precooled CH$_2$Cl$_2$ (10 mL) at −85 °C. To this solution mesitylene (243 mg, 280 μL, 2.02 mmol) was added and the reaction mixture was stirred at −85 °C for 10 min, and then slowly allowed to warm to 0 °C and stirred at this temperature for an additional 2 h. During this time the color changed to yellow-orange. Filtration via a cannula and evaporation of the solvent in dynamic vacuum yielded a yellow-orange powder that was washed with pentane (3 × 10 mL) and dried in vacuo. Yield: 0.61 g (1.063 mmol, 79%). **2-*t*Bu,Me** was stored at −35 °C under an argon atmosphere to prevent thermal degradation. ^{1}H NMR (500 MHz, 20 °C, CDCl$_3$): δ 7.05 (s, 3H, mes-CH), 4.98 (s, 1H, H$_{syn,a}$), 4.25 (s, 1H, H$_{syn,b}$), 3.65 (s, 1H, H$_{anti,b}$), 2.47 (s, 9H, mes-CH$_3$), 1.96 (s, 3H, Me), 1.01 (s, 9H, CMe$_3$). ^{13}C{^{1}H} NMR (125 Hz, 293 K, CDCl$_3$): δ 133.9 (C$_7$), 118.5 (C$_9$), 117.0 (C$_2$), 100.1 (C$_4$), 63.5 (C$_1$), 38.0 (C$_5$), 30.9 (C$_6$), 26.3 (C$_3$), 21.1 (C$_8$). Anal. Calcd for C$_{17}$H$_{27}$F$_6$PdSb: C, 35.60; H, 4.74. Found: C, 35.72; H, 4.80.

Synthesis of [(2-Me-propenylnorbornyl)Pd(μ-Cl)]$_2$ (3-Me)$_2$. The insertion product **(1-Me)$_2$** was synthesized from [(2-Me-allyl)Pd(μ-Cl)]$_2$ and NB (4 equiv) in benzene solution on heating to 50 °C according to a literature procedure.[15] Under these conditions, **(3-Me)$_2$** precipitated slowly as colorless crystals in nearly quantitative yield. These crystals were sparingly soluble in chlorinated solvents like CH$_2$Cl$_2$ and CHCl$_3$ but exhibited good solubility in pyridine to yield the monomeric, monopyridine adduct **3-Me(py)**. ^{1}H NMR (500 MHz, C$_5$D$_5$N, 20 °C): δ 4.29 (s, 1H, H$_{cis}$), 3.93 (s, 1H, H$_{trans}$), 3.15 (br.s, 1H), 3.14 (d, 1H, $^3J_{HH}$= 7 Hz, H$_8$), 2.35 (dd, 1H, $^2J_{HH}$= 16.5 Hz, $^3J_{HH}$= 10.5 Hz, H$_1$), 2.19 (dd, 1H, $^2J_{HH}$ = 16.5, $^3J_{HH}$= 5.5 Hz, H$_2$), 1.76 (s, 1H, H$_4$), 1.68 (“m”, 1H, H$_3$), 1.58 (s, 3H, CH$_3$), 1.38 (m, 1H, H$_5$), 1.22 (m, 1H, H$_9$), 1.10−1.00 (m, 3H, H$_6$, H$_6$′, H$_{10}$). ^{13}C{^{1}H} NMR (125 MHz, C$_5$D$_5$N, 23 °C): δ 126.0 (C$_2$), 75.0 (C$_1$), 59.5 (C$_9$), 47.5 (C$_4$), 44.9 (C$_3$), 44.8 (C$_8$), 42.4 (C$_5$), 34.6 (C$_7$), 30.7 (C$_6$), 29.3 (C$_{10}$), 28.1 (Me). See the Supporting Information for details regarding the attempted synthesis of **(3-Cl)$_2$**.



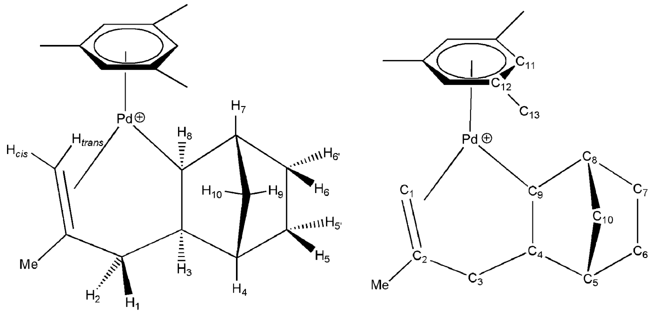
3-Me(py)



4-Me

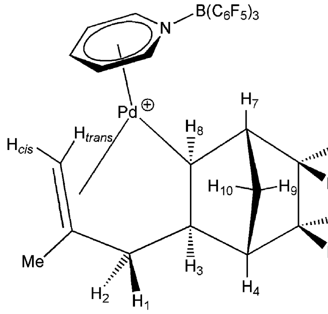
Synthesis of [(2-Me-propenylnorbornyl)Pd(py)$_2$][SbF$_6$] (4-Me). A Schlenk flask was charged with [(2-Me-propenylnorbornyl)Pd(μ-Cl)]$_2$ (**(3-Me)$_2$**) (100 mg, 0.17 mmol) of and AgSbF$_6$ (114 mg, 0.34 mmol) and the solids were dissolved in 10 mL of CH$_2$Cl$_2$ at 0 °C. To this reaction mixture pyridine (0.108 g, 1.37 mmol) was added via syringe and allowed to warm to room temperature and stirred for 2 h. The solution was filtered and taken to dryness in dynamic vacuum. The resulting white solid was washed with pentanes (3 × 10 mL) and dried in vacuo. The product was purified on recrystallization from a minimal amount of CH$_2$Cl$_2$ layered with an excess of pentane at −38 °C to give 0.15 g of **4-Me** (0.23 mmol, 68% yield) which was stored at −35 °C under an argon atmosphere to prevent thermal degradation. ^{1}H NMR (500 MHz CDCl$_3$, 23 °C): δ 8.65 (s, 4H, py-H$_m$), 7.73 (s, 2H, py-H$_p$), 7.41 (s, 4H, py-H$_o$), 4.74 (s,1H, H$_{cis}$), 4.06 (s, 1H, H$_{trans}$), 3.15 (d,1H, $^3J_{HH}$ = 7 Hz, H$_8$), 2.71 (dd, $^2J_{HH}$ = 17.6 Hz, $^3J_{HH}$ = 12 Hz, H$_1$), 2.56 (dd, $^2J_{HH}$ = 17.6 Hz, $^3J_{HH}$ = 5.5 Hz, H$_2$), 1.91 (s, 1H, H$_4$), 1.89 (d, 1H, $^2J_{HH}$ = 10 Hz, H$_{10}$), 1.70 (m, 1H, H$_3$), 1.76 (s, 3H, Me), 1.40 (m, 1H, H$_7$), 1.06 (m, 2H, H$_5$+H$_6$), 0.90 (m, 3H, H$_5$′, H$_6$′, H$_9$). ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 23 °C): δ 149.6 (C$_{11,}$ py-H$_m$), 136.5 (C$_{13}$, py-H$_p$), 123.5 (C$_{12}$, py-H$_o$), 79.5 (C$_1$), 59.6 (C$_9$), 46.9 (C$_4$), 44.1 (C$_3$), 42.3 (C$_8$), 42.1 (C$_5$), 33.7 (C$_7$), 29.3 (C$_{10}$), 28.2 (C$_6$), 27.0 (Me). (The resonance due to C$_2$ was not found and was probably obscured by a pyridine resonance.) Anal. Calcd for C$_{21}$H$_{27}$F$_6$N$_2$PdSb: C, 38.82; H, 4.19; N, 4.31. Found: C, 38.70; H, 4.21; N, 4.45.

Synthesis of [(2-Me-propenylnorbornyl)Pd(mesitylene)][SbF$_6$] (5-Me). A Schlenk flask was charged with [(2-Me-propenylnorbornyl)Pd(μ-Cl)]$_2$ (**(3-Me)$_2$**) (100 mg, 0.17 mmol) and AgSbF$_6$ (114 mg, 0.34 mmol) and dissolved in 10 mL of CH$_2$Cl$_2$ at −78 °C. Mesitylene (0.165 g, 1.37 mmol) was added via syringe and the reaction mixture was allowed to warm to 0 °C and stirred at this temperature for 2 h. The yellow suspension was filtered and the solvent was removed under dynamic vacuum. The yellow solid was washed with pentanes (3 × 10 mL) and dried in vacuo (165 mg,



5-Me

0.27 mmol, 79% yield). **5-Me** was stored at −35 °C under an argon atmosphere to prevent thermal degradation. ^{1}H NMR (500 MHz, CD_2Cl_2, 20 °C): δ 6.88 (s, 3H, aryl Mes), 3.88 (d, $^3J_{HH} = 6$ Hz, H_8), 3.80 (s, 1H, H_{cis}), 3.77 (s, 1H, H_{trans}), 2.53 (dd, 1H, $^2J_{HH} = 17$ Hz, $^3J_{HH}= 7$ Hz, H_2), 2.47 (s, 9H, me Mes), 2.28 (dd, 1H, $^2J_{HH} = 10$ Hz, $^3J_{HH} = 17$ Hz, H_1), 2.19 (s, 1H, H_7), 1.97 (s, 3H, CH_3), 1.92 (s, 1H, H_4), 1.75 (d, $^2J_{HH} = 10$ Hz, H_{10}), 1.62 (ddd, 1H, H_3), 1.5−1.4 (m, 2H, $H_5 + H_6$), 1.35 (d, $^2J_{HH} = 10$ Hz, H_{10}), 1.20 (m, 1H, H_5'), 1.07 (m, 1H, H_6'). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 20 °C): δ 135.3 (C_{12}), 130.1 (C_2), 121.6 (C_{11}), 77.0 (C_9), 70.7 (C_1), 49.5 (C_4), 48.5 (C_8), 43.6 (C_3), 42.9 (C_5), 33.7 (C_{10}), 30.1 (C_6), 28.5 (Me), 27.3 (C_7), 20.4 (C_{13}). Anal. Calcd for $C_{20}H_{29}F_6PdSb$: C, 39.27; H, 4.78. Found: C, 39.32; H, 4.82.



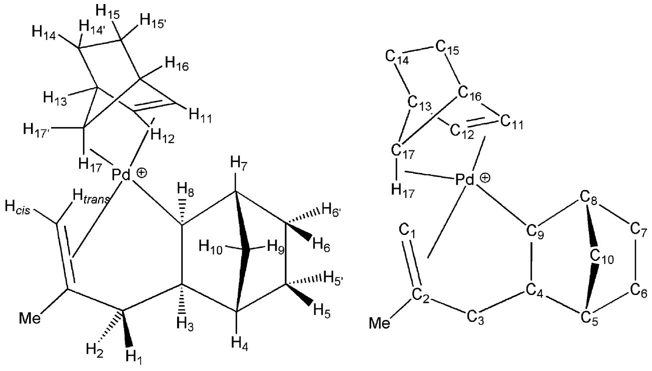
6-Me

Active Species in the Polymerization of NB by [(2-Me-propenylnorbornyl)Pd(py)$_2$][SbF$_6$] ((3-Me)$_2$) and B(C_6F_5)$_3$ by NMR (6-Me). A screw-cap NMR tube was charged with 10 mg (0.015 mmol) of **(3-Me)$_2$** and 4 equiv (0.036 g, 0.060 mmol) of $B(C_6F_5)_3$ and dissolved in CD_2Cl_2 and characterized by ^{19}F NMR (376.5 MHz CD_2Cl_2, 23 °C): Free $B(C_6F_5)_3$: δ −127.2 (d, $^3J_{FF} =$ 19 Hz, *o*-F), −142.9 (br.s, *p*-F), −160.4 (t, *m*-F). Py*$B(C_6F_5)_3$: δ−131.9 (d, $^3J_{FF} = 19$ Hz, *o*-F), −157.4 (t, $^3J_{FF} = 21$ Hz, *p*-F), −164.0 (td, $^3J_{FF} = 19$ and 21 Hz, *m*-F). (borane-pyridine capped Pd species) δ −139.2 (d, $^3J_{FF} = 19$ Hz, *o*-F), −154.5 (t, $^3J_{FF} = 21$ Hz, *p*-F), −162.7 (td, $^3J_{FF} = 19$ and 21 Hz, *m*-F). ^{1}H NMR (400 MHz CD_2Cl_2, 23 °C): δ 8.63 (d, $^3J_{HH} = 4.8$ Hz, 2H, py-H_m), 8.24 (t, $^3J_{HH} = 7.6$ Hz, 1H, py-H_p), 7.74 (t, $^3J_{HH} = 6.8$, 2H, py-H_o), 4.54 (bs, 2H, H_{cis}+H_{trans}), 4.08 (bs, 1H, H_8), 2.60 (dd, $^2J_{HH} = 11$ Hz, $^3J_{HH} = 6$ Hz, 1H, H_2), 2.28 (dd, $^2J_{HH} = 11$ Hz,$^3J_{HH} = 18$ Hz, 1H, H_1) 2.12 (s, 3H, Me), 2.0 (s, 1H, H_7), 1.93(bs, 1H, H_{10}), 1.78 (bs, 1H, H_4), 1.5 (m, 1H, H_3), 1.4−1.0 (5H, H_9, H_6, H_6', H_5, H_5').

Series of Low-Temperature VT NMR Studies of the Reaction of Cationic (allyl)Pd(II) Catalysts with NB. In Situ Generation of [(2-Me-propenylnorbornyl)Pd(mesitylene)][SbF$_6$] (5-Me) from [(2-Me allyl)Pd(mesitylene)][SbF$_6$] (2-Me). In a screw-cap NMR tube **2-Me** (10 mg, 1.9 × 10^{-2} mmol) was dissolved in dry degassed $CDCl_2F$ at −140 °C, and 1 equiv of a NB stock solution (34 μL, 1.9 × 10^{-2} mmol) in CD_2Cl_2 was added. The reaction mixture was inserted into a precooled NMR probe (−120 °C). The ^{1}H NMR spectrum confirmed that the NB insertion was instantaneous and the NMR spectra agreed with independently synthesized **5-Me**.

In Situ Generation of 7-Me from [(2-Me-allyl)Pd(mesitylene)][SbF$_6$] (2-Me) or 5-Me. In a screw-cap NMR tube **2-Me** (20 mg, 3.8 × 10^{-2} mmol) was dissolved in dry degassed $CDCl_2F$ at −140 °C, and 1.9 equiv of a NB stock solution (130 μL, 7.2 × 10^{-2} mmol) in CD_2Cl_2 was added. The reaction mixture was inserted into a precooled NMR probe (−120 °C). The ^{1}H NMR spectrum confirmed that the NB insertion was instantaneously and one NB molecule displaced the mesitylene ligand to form **7-Me**.

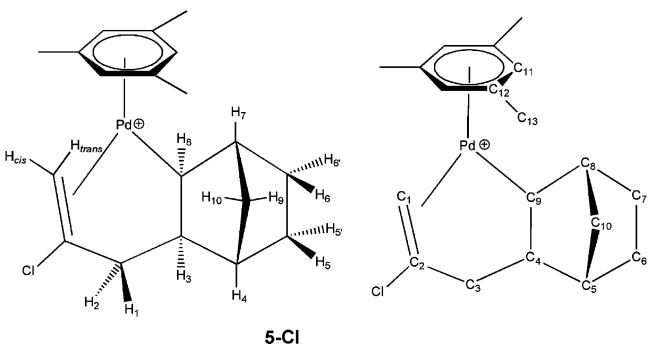
Alternatively, **7-Me** was generated from **5-Me** on NB addition: In a screw-cap NMR tube **2-Me** (20 mg, 3.27 × 10^{-2} mmol) was dissolved in dry degassed $CDCl_2F$ at −140 °C, and ca. 0.9 equiv (50 μL, 2.94 × 10^{-2} mmol) of a NB stock solution in CD_2Cl_2 was added. The reaction mixture was inserted into a precooled NMR probe (−120 °C). The NMR spectra confirmed the formation of **7-Me** and mesitylene displacement. Single crystals suitable for an X-ray diffraction experiment were grown at −80 °C from this solution on addition of a layer of pentane.



7-Me

^{1}H NMR (500 MHz, $CDCl_2F$, −120 °C): δ 6.19 (s, 1H, H_{11}/H_{12}), 5.81 (s, 1H, H_{12}/H_{11}), 5.02 (s, 1H, H_{cis}), 4.87 (s, 1H, H_{trans}), 4.46 (br.s, 1H, H_8), 3.48 (br.s., 2H, H_{13}+H_{16}), 2.74 (dd, 1H, H_2, coupling not resolved), 2.63 (dd, $^2J_{HH} = 18$ Hz, $^3J_{HH} = 10$ Hz, 1H, H_1), 2.06 (s, 1H, H_4), 1.93 (br.s., 2H, H_3+H_7), 1.77−1.71 (m, 5H, H_{10}, H_{14}, H_{14}', H_{15}, H_{15}'), 1.52 (d, $^2J_{HH} = 11.5$ Hz, 1H, H_{17}'), 1.50 (m, 1H, H_4), 1.32−1.30 (m, 2H, H_5+H_6), 1.23 (d, 1H, $^2J_{HH} = 10$ Hz, H_9), 1.10−1.07 (m, 2H, H_5'+H_6'), −1.28 (d, $^2J_{HH} = 11.5$ Hz, H_{17}). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_2F$, −120 °C): δ 154.6 (C_2), 125.3 (C_{11}/C_{12}), 116.7 (C_{12}/C_{11}), 90.5 (C_1), 84.9 (C_9), 52.1 (C_8), 45.3 (C_{13}+C_{16}), 44.9 (C_4), 44.6 (C_5), 42.5 (C_{17}), 42.4 (C_3), 34.5 (C_{10}), 28.5 (Me), 27.9 (C_7), 27.2 (C_6), 24.0 (C_{14}/C_{15}), 24.1 (C_{15}/C_{14}).

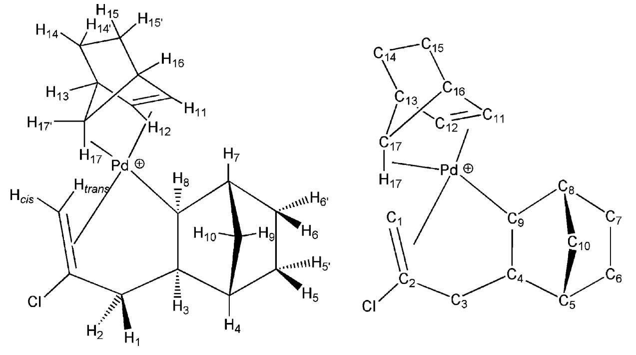
In Situ Generation of [(2-Cl-propenylnorbornyl)Pd(mesitylene)][SbF$_6$] (5-Cl) from [(2-Cl-allyl)Pd(mesitylene)][SbF$_6$] (2-Cl). In a screw-cap NMR tube, [(2-Cl-allyl)Pd(mesitylene)][SbF$_6$] **(2-H)** (0.01 g, 9.53 × 10^{-3} mmol) was dissolved in dry degassed $CDCl_2F$ at −130 °C and a stock solution of NB (32 μL, 9.53 × 10^{-2} mmol, ca. 1 equiv.) in CD_2Cl_2 was added. The reaction mixture was inserted into a precooled NMR probe (−120 °C). The insertion was instantaneous under these conditions and **5-Cl** was characterized by various NMR techniques.



5-Cl

^{1}H NMR (500 MHz, $CDCl_2F$, −120 °C): δ 6.92 (s, 3H, aryl Mes), 4.21 (s, 1H, H_{cis}), 3.88 (d, $^3J_{HH} = 9$ Hz, H_8), 3.87 (s, 1H, H_{trans}), 2.97 (dd, 1H, H_2, coupling not resolved), 2.56 (s, 9H, me Mes), 2.73 (dd, 1H, H_1), 2.33 (s, 1H, H_7), 2.06 (s, 1H, H_4), 1.86 (d, $^2J_{HH} = 9$ Hz, H_{10}), 1.79 (ddd, 1H, H_3), 1.53 (m, 1H, H_6), 1.50 (m, 1H, H_5), 1.48 (d, $^2J_{HH} = 9$ Hz, H_{10}), 1.26 (m, 1H, H_5'), 1.13 (m, 1H, H_6'). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_2F$, −120 °C): δ 134.8 (C_{12}), 126.8 (C_2), 122.1 (C_{11}), 77.4 (C_9), 68.0 (C_1), 49.4 (C_4), 48.8 (C_8), 46.6 (C_3), 42.6 (C_5), 33.5 (C_{10}), 30.0 (C_6), 26.8 (C_7), 20.4 (C_{13}).

In Situ Generation of 7-Cl from [(2-Cl-allyl)Pd(mesitylene)][SbF$_6$] (2-Cl). In a screw-cap NMR tube, [(2-Cl-allyl)Pd(mesitylene)][SbF_6] **(2-Cl)** (0.02 g, 1.91 × 10^{-2} mmol) was dissolved in dry degassed $CDCl_2F$ at −130 °C and a stock solution of NB (100 μL, 3.06 × 10^{-2} mmol, ca. 1.6 equiv) in CD_2Cl_2 was added. The reaction mixture was inserted into a precooled NMR probe (−120 °C). The insertion was instantaneous under these conditions and **7-Cl** was characterized by various NMR techniques.

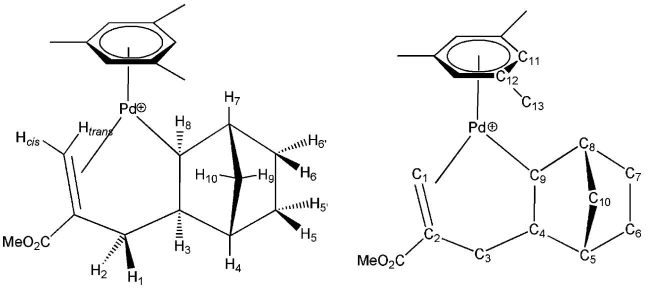


7-Cl

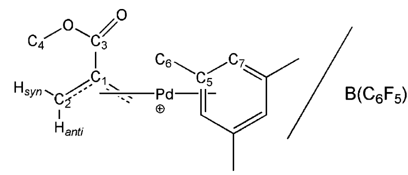
^{1}H NMR (500 MHz, $CDCl_2F$, −120 °C): δ 6.37 (s, 1H, H_{11}/H_{12}), 5.97 (s, 1H, H_{12}/H_{11}), 5.40 (s, 1H, H_{cis}), 5.32 (s, 1H, H_{trans}), 3.61 (br.s., 2H, H_{13}+H_{16}), 3.54 (d, $^3J_{HH} = 9$ Hz, H_8), 3.18 (dd, 1H, H_2, coupling not resolved), 3.01 (dd, 1H, H_1, coupling not resolved), 2.07 (ddd, 1H, H_3, coupling not resolved), 1.89 (d, $^2J_{HH} = 9$ Hz, H_{10}), 1.80 (s, 1H, H_7), 1.65 (d, $^2J_{HH} = 11.5$ Hz, H_{17}'), 1.60 (m, 1H, H_6), 1.58 (m, 1H, H_5), 1.57 (s, 1H, H_4), 1.52−1.49 (m. 4H, H_{14}, H_{14}', H_{15}, H_{15}'), 1.48 (d, $^2J_{HH} = 9$ Hz, H_9), 1.26 (m, 1H, H_5'), 1.12 (m, 1H, H_6'), −0.94 (d, $^2J_{HH} = 11.5$ Hz, H_{17}). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_2F$, −120 °C): δ 143.6 (C_2), 126.8 (C_{11}/C_{12}), 118.2 (C_{12}/C_{11}), 90.6 (C_1), 89.4 (C_9), 53.1 (C_8), 48.8 (C_4), 46.6 (C_{10}), 44.8 (C_{13}/C_{16}), 44.7 (C_3), 44.6 (C_{16}/C_{13}), 43.2 (C_{17}), 42.4 (C_5), 34.3 (C_{14}/C_{15}), 33.5 (C_{15}/C_{14}), 30.4 (C_7), 26.8 (C_6).

In Situ Generation of [(2-MeO$_2$C-propenylnorbornyl)Pd(mesitylene)][SbF$_6$] (5-CO$_2$Me) from [(2-MeO$_2$C-allyl)Pd(mesitylene)][SbF$_6$] (2-CO$_2$Me). In a screw-cap NMR tube, [(2-CO_2Me-allyl)Pd(mesitylene)][SbF_6] **(2-CO$_2$Me)** (0.021 g, 3.74 × 10^{-2} mmol) was dissolved in dry degassed $CDCl_2F$ at −130 °C and a stock solution of NB (250 μL, 1.87 × 10^{-1} mmol, ca. 5 equiv) in CD_2Cl_2 was added. The reaction mixture was inserted into a precooled NMR probe (−120 °C). In contrast to the observations for **2-Me** and **2-Cl**, the mesitylene displacement and insertion was not instantaneously. Under these conditions, **5-CO$_2$Me** was the major species in solution with minor amounts of **5-CO$_2$Me** remaining together with a small fraction of agostic complex **7-CO$_2$Me**. Warming to −98 °C resulted in disappearance of **2-CO$_2$Me** and NMR evidence showed that the bound NB of **7-CO$_2$Me** was in rapid exchange with free NB. Further warming to −64 °C resulted in formation of poly(norbornene) with **5-CO$_2$Me** as the sole observable Pd species in solution which was characterized via a variety of 1D and 2D NMR experiments.

^{1}H NMR (500 MHz, $CDCl_2F$, −86 °C): δ 6.79 (s, 3H, aryl Mes), 4.56 (s, 1H, H_{cis}), 4.19 (s, 1H, H_{trans}), 4.18 (d, coupling unresolved due to signal overlap, H_8), 3.80 (s, 3H, OCH_3), 2.69 (dd, 1H, H_2, $^2J_{HH} = 17$ Hz, $^3J_{HH} = 7$ Hz), 2.67 (dd, 1H, $^2J_{HH} = 17$ Hz, $^3J_{HH} = 10$ Hz, 1H, H_1), 2.36 (s, 9H, me Mes), 2.23 (s, 1H, H_7), 1.95 (s, 1H, H_4), 1.73 (d, $^2J_{HH} = 10$ Hz, H_{10}), 1.69 (ddd, coupling not resolved, 1H, H_3), 1.42 (m, 2H, H_5+H_6), 1.35 (d, $^2J_{HH} = 10$ Hz, H_{10}), 1.19 (m, 1H, H_5'), 1.07 (m, 1H, H_6'). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_2F$, −86 °C): δ 167.4 (CO_2Me), 134.4 (C_{12}), 122.6 (C_2), 121.5 (C_{11}), 84.6 (C_9), 74.6 (C_1), 53.9 (CO_2Me), 49.6 (C_8), 49.4 (C_4), 42.9 (C_5), 36.1 (C_3), 33.4 (C_{10}), 30.0 (C_6), 26.8 (C_7), 19.8 (C_{13}).



5-CO$_2$Me

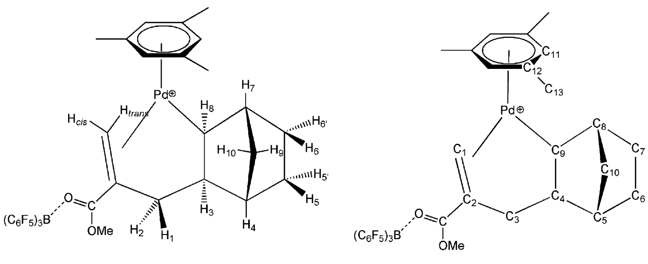


2-CO$_2$Me/B(C$_6$F$_5$)$_3$

Active Species in the Polymerization of NB by [(2-MeO$_2$C-allyl)Pd(mesitylene)][SbF$_6$] Complex (2-CO$_2$Me) and B(C$_6$F$_5$)$_3$ by NMR. In a screw-cap NMR tube, [(2-MeO_2C-allyl)Pd(mesitylene)][SbF_6] **(2-CO$_2$Me)** (0.021 g, 3.74 × 10^{-3} mmol) and $B(C_6F_5)_3$ (0.029 g, 5.66 × 10^{-3} mmol, 1.5 equiv) were dissolved in dry degassed $CDCl_2F$ at −130 °C to form a light yellow solution. ^{1}H NMR (500 MHz, $CDCl_2F$, −110 °C): δ 7.11 (s, 3H, mes-CH), 4.79 (s, 2H, H_{syn}), 3.86 (s, 3H, CH_3), 3.32 (s, 2H, H_{anti}), 2.44 (s, 9H, mes-CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2, −110 °C): δ 167.9 (C_3), 132.9 (C_5), 115.9 (C_7), 106.9 (C_1), 64.9 (C_2), 56.4 (C_4), 20.7 (C_6). $^{13}C\{^1H\}$ NMR chemical shifts corresponding to $B(C_6F_5)_3$ have been omitted.

In Situ Generation of [(2-MeO$_2$C-propenylnorbornyl)Pd(mesitylene)][SbF$_6$]*B(C$_6$F$_5$)$_3$ (5-CO$_2$Me/B(C$_6$F$_5$)$_3$) from [(2-MeO$_2$C-allyl)Pd(mesitylene)][SbF$_6$]/B(C$_6$F$_5$)$_3$ (2-CO$_2$Me/B(C$_6$F$_5$)$_3$). In a screw-cap NMR tube, [(2-MeO_2C-allyl)Pd(mesitylene)][SbF_6] (**2-CO$_2$Me**) (0.021 g, 3.74 × 10^{-3} mmol) and $B(C_6F_5)_3$ (0.029 g, 5.66 × 10^{-3} mmol, 1.5 equiv) were dissolved in dry degassed $CDCl_2F$ at −130 °C and a stock solution of NB (250 μL, 1.87 × 10^{-1} mmol, ca. 5 equiv) in CD_2Cl_2 was added. The bright yellow reaction mixture was inserted into a precooled NMR probe (−120 °C). Similar to **2-CO$_2$Me** mesitylene displacement and insertion was not instantaneously. The obtained reaction mixture was complex and contained several species some of which were undergoing exchange processes: Unreacted starting material (**1-CO$_2$Me**) (as the dominant species), free NB, the mesitylene-capped first-insertion product (**2-CO$_2$Me**) and the NB-capped-first insertion product (**7-CO$_2$Me**). After warming to 220 K, polymer formed and all free NB was consumed. The only Pd containing species was **5-CO$_2$Me/B(C$_6$F$_5$)$_3$**, and it was characterized via a variety of 1D and 2D NMR experiments.

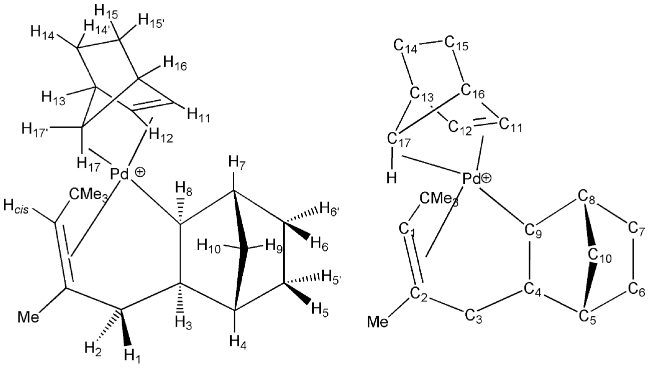
^{1}H NMR (500 MHz, $CDCl_2F$, 0 °C): δ 6.88 (s, 3H, aryl Mes), 4.62 (s, 1H, H_{cis}), 4.29 (d, $^3J_{HH} = 9$ Hz, H_8), 4.33 (s, 1H, H_{trans}), 3.85 (s, 3H, OCH_3), 2.73 (dd, $^2J_{HH} = 17$ Hz, $^3J_{HH} = 10$ Hz, 1H, H_1), 2.69 (dd, $^2J_{HH} = 17$ Hz, $^3J_{HH} = 7$ Hz, 1H, H_2), 2.45 (s, 9H, me Mes), 2.28 (s, 1H, H_7), 1.97 (s, 1H, H_4), 1.80 (d, $^2J_{HH} = 10$ Hz, H_{10}), 1.75 (ddd, coupling not resolved, 1H, H_3), 1.47 (m, 2H, H_5+H_6), 1.40 (d, $^2J_{HH} = 10$ Hz, H_{10}), 1.27 (m, 1H, H_5'), 1.12 (m, 1H, H_6'). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_2F$, −86 °C): δ 168.1



5-CO_2Me/$B(C_6F_5)_3$

(CO_2Me), 134.3 (C_{12}), 122.8 (C_2), 121.5 (C_{11}), 84.9 (C_9), 74.5 (C_1), 53.7 (CO_2Me), 49.7 (C_8), 49.3 (C_4), 42.8 (C_5), 36.2 (C_3), 33.3 (C_{10}), 30.2 (C_6), 27.0 (C_7), 19.8 (C_{13}). $^{13}C\{^1H\}$ NMR chemical shifts corresponding to $B(C_6F_5)_3$ have been ommited. ^{19}F NMR (470.6 MHz, $CDCl_2F$, −86 °C): Free $B(C_6F_5)_3$: δ −127.6 (d, $^3J_{FF} = 21$ Hz, *o*-F), −142.7 (t, $^3J_{FF} = 21$ Hz, *p*-F), −160.6 (t, $^3J_{FF} = 21$ Hz, *m*-F). **5-CO_2Me/$B(C_6F_5)_3$**: δ −135.0 (d, $^3J_{FF} = 20$ Hz, *o*-F), −156.7 (t, $^3J_{FF} = 20$ Hz, *p*-F), −164.0 (t, $^3J_{FF} = 20$ Hz, *m*-F).

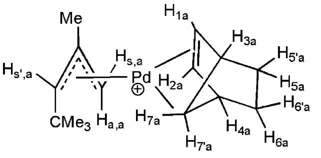
In Situ Generation of 7-*t*Bu,Me from [(1-tBu-2-Me-allyl)Pd-(mesitylene)][SbF_6] (2-tBu,Me). In a screw-cap NMR tube, **2-*t*Bu,Me** (0.021 g, 3.15×10^{-2} mmol) was dissolved in dry degassed CD_2Cl_2 at −86 °C and a stock solution of NB (330 μL, 6.30×10^{-2} mmol, 2 equiv) in CD_2Cl_2 was added. The reaction mixture was inserted into a precooled NMR probe (−86 °C). The mesitylene displacement was instantaneous, but **7-*t*Bu,Me** was formed besides the two preinsertion species **8a,b-*t*Bu,Me** which converted slowly to **7-*t*Bu,Me** at this temperature. **7-*t*Bu,Me** was characterized by various NMR techniques.



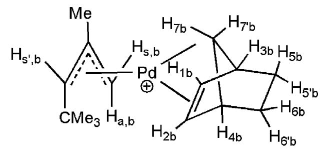
7-*t*Bu,Me

^1H NMR (500 MHz, CD_2Cl_2, −86 °C): δ 6.35 (s, 1H, H_{11}/H_{12}), 5.90 (s, 1H, H_{12}/H_{11}), 5.49 (s, 1H, H_{cis}), 4.81 (br.s, 1H, H_8), 3.44 (s, 1H, H_{13}/H_{16}), 3.32 (s, 1H, H_{16}/H_{13}), 2.64−2.59 (m, 2H, H_1+H_2), 2.07 (ddd, 1H, H_3, coupling not resolved), 2.04 (s, 1H, H_7), 1.55 (d, 1H, H_{10}, coupling not resolved), 1.53−1.51 (m. 4H, H_{14}, H_{14}', H_{15}, H_{15}'), 1.50 (m, 1H, H_6), 1.48 (s, 1H, H_4), 1.28 (m, 1H, H_5), 1.27 (d, 1H, H_9, coupling not resolved), 1.12 (m, 1H, H_5'), 1.08 (m, 1H, H_6'), −0.94 (d, $^2J_{HH} = 12$ Hz, H_{17}). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2, −86 °C): δ 136.5 (C_2), 121.3 (C_{11}/C_{12}), 115.4 (C_{12}/C_{11}), 126.0 (C_1), 95.2 (C_9), 64.6 (C_8), 44.9 (C_{13}/C_{16}), 44.1 (C_{16}/C_{13}), 43.5 (C_4), 42.1 (C_{17}), 41.9 (C_5), 35.8 (C_3), 35.7 (CMe_3), 33.6 (C_{10}), 32.3 (CMe_3), 27.4 (C_7), 26.8 (C_6). 25.5 (Me), 24.8 (C_{14}/C_{15}), 24.5 (C_{15}/C_{14}),

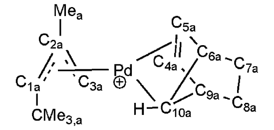
In Situ Generation of [(2-tBu-2-Me-allyl)Pd(norbornene)]-[SbF_6] (8a-*t*Bu,Me and 8b-*t*Bu,Me). In a screw-cap NMR tube, **2-*t*Bu,Me** (0.021 g, 3.15×10^{-2} mmol) was dissolved in dry degassed $CDCl_2F$ at −120 °C and then frozen in liquid N_2. A stock solution of NB (25 μL, 1.78×10^{-2} mmol, 0.6 equiv) in CD_2Cl_2 was added, the mixture warmed to −140 °C, quickly shaken and inserted into a precooled NMR probe at −120 °C. Under these conditions ca. 40% of unreacted **2-*t*Bu,Me** remained in solution, while the two preinsertion species, **8a-*t*Bu,Me** and **8b-*t*Bu,Me**, were formed in a ca. 1:1 ratio (>50%) and **7-*t*Bu,Me** was formed in <10%. Attention to detail had to be observed, otherwise **7-*t*Bu,Me** readily formed in significant quantity at the expense of **8a-*t*Bu,Me** and **8b-*t*Bu,Me**. Interestingly, even at −130 °C the two preinsertion species exchange with each other as substantiated by a significant line broadening relative to the line shapes for **2-*t*Bu,Me** at the same temperature.



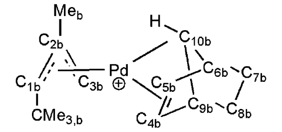
8a-*t*Bu,Me



8b-*t*Bu,Me



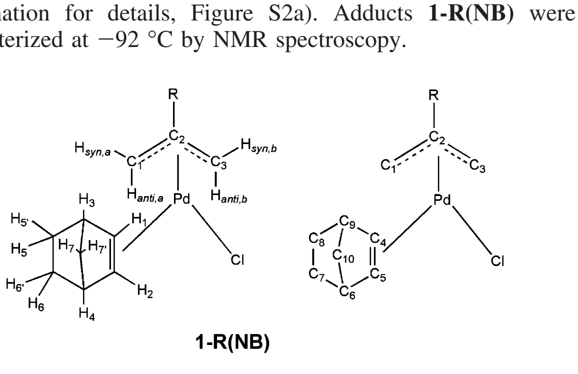
8a-*t*Bu,Me



8b-*t*Bu,Me

The ^1H and ^{13}C NMR resonances corresponding to the allyl-moiety in both isomers, **8a-*t*Bu,Me** and **8b-*t*Bu,Me**, are identical at −120 °C, although slightly broadened. ^1H NMR (500 MHz, $CDCl_2F$, −120 °C): **8a-*t*Bu,Me** or **8b-*t*Bu,Me:** δ 6.49 (s, 1H, $H_{s',a}$), 6.00 (s, 1H, H_{1a}/H_{2a}), 5.47 (s, 1H, $H_{s,a}$), 5.18 (s, 1H, H_{2a}/H_{1a}), 3.84 (s, 1H, $H_{a,a}$), 3.36 (s, 1H, H_{3a}/H_{4a}), 3.00 (s, 1H, H_{4a}/H_{3a}), 1.82−1.73 (m, 2H, H_{5a}, H_{6a}), 1.72 (s, 3H, Me), 1.40−1.30 (m, 2H, H_{5a}', H_{6a}'),1.10 (s, 9H, CMe_3), 0.90 (d, $^2J_{HH} = 9.0$ Hz, $^1J_{CH} = 138$ Hz, 1H, $H_{7'a}$), −0.19 (d, $^2J_{HH} = 9.0$ Hz, $^1J_{CH} = 135$ Hz, 1H, H_{7a}). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_2F$, −120 °C): δ 119.1 (C_{1a}), 117.4 (C_{2a}), 107.7 (C_{4a}/C_{5a}), 100.1 (C_{5a}/C_{4a}), 76.6 (C_{3a}), 44.6 (C_{6a}/C_{9a}), 43.5 (C_{9a}/C_{6a}), 41.8 (C_{10a}), 38.1 (CMe_3), 32.3 ($CMe_{3,a}$), 25.5 (Me_a) 25.2 (C_{7a}/C_{8a}), 24.4 (C_{8a}/C_{7a}). **8b-*t*Bu,Me** or **8b-*t*Bu,Me:** δ 6.49 (s, 1H, $H_{s',b}$), 5.59 (s, 1H, H_{1b}/H_{2b}), 5.47 (s, 1H, $H_{s,b}$), 4.96 (s, 1H, H_{2b}/H_{1b}), 3.84 (s, 1H, $H_{a,b}$), 3.47 (s, 1H, H_{3b}/H_{4b}), 3.18 (s, 1H, H_{4b}/H_{3b}), 1.82−1.73 (m, 2H, H_{5b}, H_{6b}), 1.72 (s, 3H, Me), 1.40−1.30 (m, 2H, H_{5b}', H_{6b}'), 1.10 (s, 9H, CMe_3), 0.77 (d, $^2J_{HH} = 9.5$ Hz, $^1J_{CH} = 139$ Hz, 1H, $H_{7'b}$), 0.22 (d, $^2J_{HH} = 9.5$ Hz, $^1J_{CH} = 131$ Hz, 1H, H_{7b}). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_2F$, −120 °C): δ 119.1 (C_{1b}), 117.4 (C_{2b}), 107.2 (C_{4b}/C_{5b}), 103.0 (C_{5b}/C_{4b}), 76.6 (C_{3b}), 44.7 (C_{6b}/C_{9b}), 44.1 (C_{9b}/C_{6b}), 42.9 (C_{10b}), 38.1 (CMe_b), 32.3 ($CMe_{3,b}$), 25.5 (Me_b) 24.9 (C_{7b}/C_{8b}), 24.8 (C_{8b}/C_{7b}).

Low-Temperature NMR Study of the Reactions of [(2-Me-allyl)Pd(μ-Cl)]$_2$ and [(2-Cl-allyl)Pd(μ-Cl)]$_2$ with NB. A screw-cap NMR tube was charged with either [(2-Me-allyl)Pd(μ-Cl)]$_2$ (0.01 g, 1.61×10^{-2} mmol) or [(2-Cl-allyl)Pd(μ-Cl)]$_2$ (0.01 g, 1.61×10^{-2} mmol). The complexes were dissolved in CD_2Cl_2 (500 μL) at −78 °C, and 2.5 equiv (75 μL, 2.42×10^{-2} mmol) of NB stock solution in CD_2Cl_2 were added to each solution. Since the formed adducts were less soluble than the starting dimers at low temperature, an internal standard (1,3,5-$(F_3C)_3C_6H_3$: 10 μL, 0.053 mmol) was added to monitor changes in concentration of each species. The interaction of NB and [(2-R-allyl)Pd(μ-Cl)]$_2$ was monitored by ^1H NMR spectroscopy from −86 to +5 °C (see Supporting Information for details, Figure S2a). Adducts **1-R(NB)** were characterized at −92 °C by NMR spectroscopy.



1-R(NB)

NB Adduct of [(2-Me-allyl)Pd(μ-Cl)]$_2$ (**1-Me(NB)**): ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, −80 °C): δ 5.26 (d, $^3J_{HH}$ = 3.5 Hz, 1H, H_1/H_2), 5.13 (d, $^3J_{HH}$ = 3.5 Hz 1H, H_1/H_2), 4.43 (s, 1H, $H_{syn,a}/H_{syn,b}$), 4.35 (s, 1H, $H_{anti,a}/H_{anti,b}$), 3.47 (s, 1H, $H_{syn,b}/H_{syn,a}$), 2.94 (s, 1H, H_3/H_4), 2.90 (s, 1H, H_3/H_4), 2.76 (s, 1H, $H_{anti,b}/H_{anti,a}$), 1.84 (s, 3H, Me), 1.52−0.72 (6H, $H_{5,5',6,6',7,7'}$). ^{13}C{^{1}H} NMR (125 MHz, CD$_2$Cl$_2$, −80 °C): 128.1 (C_2), 108.1 (C_4/C_5), 106.0 (C_5/C_4), 71.9 (C_1/C_3), 65.5 (C_3/C_1), 48.4 (C_{10}), 43.0 (C_9/C_6), 41.8 (C_6/C_9), 24.6 (Me), 24.9 (C_7/C_8), 24.7 (C_8/C_7). The thermodynamic parameters of this equilibrium process were evaluated between 180 and 215 K; see Supporting Information for details, Figure S3.

NB Adduct of [(2-Cl-allyl)Pd(μ-Cl)]$_2$ (**1-Cl(NB)**): ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, −80 °C): δ 5.40 (s, 1H, H_1/H_2), 5.32 (s, 1H, H_1/H_2), 4.78 (s, 1H, $H_{syn,a}/H_{syn,b}$), 4.65 (s, 1H, $H_{anti,a}/H_{anti,b}$), 3.87 (s, 1H, $H_{syn,b}/H_{syn,a}$), 3.17 (s, 1H, $H_{anti,b}/H_{anti,a}$), 2.98 (s, 1H, H_3/H_4), 2.93 (s, 1H, H_3/H_4), 1.6−0.72 (6H, $H_{5,5',6,6',7,7'}$). ^{13}C{^{1}H} NMR (125 MHz, CD$_2$Cl$_2$, −80 °C): 126.0 (C_2), 109.2 (C_4/C_5), 107.7 (C_5/C_4), 77.9 (C_1/C_3), 65.8 (C_3/C_1), 48.4 (C_{10}), 43.2 (C_9/C_6), 43.0 (C_6/C_9), (bridge head), 24.4 (C_7/C_8), 24.3 (C_8/C_7).

Polymerization Procedures. General Procedure for the Polymerization of NB with 2-Cl and 2-CO$_2$Me. A Schlenk tube was charged with **2-Cl** or **2-CO$_2$Me** (2.0×10^{-5} mol) and dissolved in 2.0 mL of CH$_2$Cl$_2$. Then, 7.0 mL of methylcyclohexane was added and the solution placed in a cold bath (see Table 1 and 2 for various temperatures) and allowed to equilibrate at the specified temperature for 15−20 min. A similarly cold NB stock solution (234 equiv, 1.0 mL) in a methylcyclohexane (4.67 M, 0.879 g, 4.58 mmol) was then added for a total volume of 10.0 mL. The polymerization was monitored at various times and quenched with acidified MeOH. The poly(norbornene) was filtered, washed with acetone, and dried in vacuo overnight at 50 °C after which the conversion was determined gravimetrically. Molecular weights and MWDs were determined by high-temperature GPC.

General Procedure for the Polymerization of NB with 2-CO$_2$Me and B(C$_6$F$_5$)$_3$. Essentially, the same procedure as described for **2-CO$_2$Me** was used, except that the catalyst **2-CO$_2$Me** (2.0×10^{-5} mol) and B(C$_6$F$_5$)$_3$ ($4.\ 0 \times 10^{-5}$ mol) were dissolved in 2.0 mL of CH$_2$Cl$_2$ and stirred at 0 °C for 10 min before NB addition.

General Procedure for the Polymerization of NB with 4-Me and B(C$_6$F$_5$)$_3$. A Schlenk tube was charged with **4-Me** (0.01 g, 1.68×10^{-5} mol) and 4 equiv of B(C$_6$F$_5$)$_3$ (0.02 g, 3.3×10^{-5} mol) in the drybox. To dissolve catalyst and cocatalyst 2 mL of CH$_2$Cl$_2$ were added, at which point the colorless solution turned bright yellow, followed by the polymerization solvent (methylcyclohexane) and NB stock solution (to form a total volume of 10 mL) at room temperature. The polymerization was quenched by injection of MeOH then filtered. Polymer was dried overnight in a vacuum oven at 80 °C after which conversion was determined gravimetrically. Molecular weights and MWDs were determined by high-temperature GPC analysis.

General Procedure for the Polymerization of NB with 5-Me. A Schlenk tube was charged with **5-Me** (0.01 g, 1.6×10^{-5} mol) in the drybox. To dissolve the catalyst, 2 mL of CH$_2$Cl$_2$ was added, followed by polymerization solvent (methylcyclohexane) and NB stock solution (to form a total volume of 10 mL) at room temperature. Polymerization was quenched by injection of MeOH and filtered. Polymer was dried overnight in a vacuum oven at 80 °C after which conversion was determined gravimetrically. Molecular weights and MWDs were determined by high-temperature GPC analysis.

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Supporting Information Available: CIF files, tables giving crystallographic data for **(3-Me)$_2$**, **4-Me**, **5-Me**, **7-Me**, and **7-*t*Bu,Me**, ^{1}H NMR studies on the adduct formation between **(1-Me)$_2$** and NB, thermodynamic parameters on this adduct formation, ^{1}H NMR spectrum of **5-Me**, ^{1}H and ^{13}C NMR investigations on **7-Me**, ^{1}H NMR spectra of the preinsertion species **8a,b-*t*Bu,Me** and the attempted independent synthesis of **(3-Cl)$_2$** and **5-Cl**. This material is available free of charge via the Internet at http://pubs.acs.org.

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