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Reactions of Cationic Palladium α-Diimine Complexes with Nitrogen-Containing Olefins: Branched Polyethylene with Carbazole Functionalities

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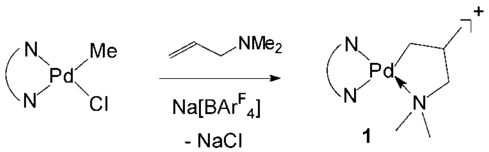
The reactivity of three nitrogen-containing olefins with a cationic (α-diimine)Pd−Me species was studied to evaluate possibilities for their catalytic copolymerization with ethylene. Allyl dimethyl amine gives 1,2-insertion into the Pd−Me bond, but the resulting five-membered chelate is inert toward ethylene. Olefins bearing carbazole substituents insert to form three-membered chelate complexes after a chain-walking process. These chelates are reactive toward ethylene, and *N*-pentenylcarbazole was successfully copolymerized with ethylene to yield branched polyethylene copolymers bearing carbazole functionalities. The fluorescence of these copolymers is dependent on the amount of incorporated comonomer.

Introduction

The introduction of (polar) functionalities into polyolefin materials by the catalytic copolymerization of simple olefins such as ethylene and propylene with olefins bearing functionalities has been a research topic of considerable interest.[1] Although conceptionally straightforward, its practical implementation has to contend with two considerable difficulties: (a) competition of the functionality with the olefin for binding to the catalyst metal center (exacerbated after comonomer insertion by the possibility of intramolecular coordination to give stable chelates) and (b) irreversible reactions of the polar functionality with the polarized metal–carbon bond in the catalyst. A fruitful approach has been to use a soft Lewis-acidic metal in the catalyst species, and the cationic palladium catalyst $[\mathrm{(DAD)PdMe(OEt_2)}][\mathrm{BAr^F{}_4}]$ (DAD = ArN=CMe−CMe=NAr, Ar = 2,6-$i\mathrm{Pr_2C_6H_3}$; $\mathrm{Ar^F}$ = 3,5-$\mathrm{(CF_3)_2C_6H_3}$) was successfully used to copolymerize ethylene with methyl acrylate to yield branched copolymers, albeit at modest productivities.[2] Subsequently, this catalyst system has been employed with various functionalized comonomers, with varying rates of success.[3] In order to reveal the potential of this approach, we have tried to study in a more systematic fashion the reactivity of the cationic $[\mathrm{(DAD)PdMe}]^+$ species with functionalized olefins. Earlier we described the reactivity toward the oxygen-containing olefins allyl methyl ether and acrolein dimethyl acetal, where the latter could successfully be copolymerized with ethylene.[4] Here we describe the reactivity toward some nitrogen-containing olefins. Results include the characterization of an unusual type of three-membered chelate complex and the successful synthesis of branched polyethylene copolymers bearing carbazole functionalities.

Scheme 1



Results and Discussion

Reaction with Allyl Dimethyl Amine (ADA). Using the method described by Brookhart and co-workers to generate chelate complexes resulting from methyl acrylate insertion into the Pd−Me bond,[2b] (DAD)PdMeCl (DAD = ArN=CMe−CMe=NAr, Ar = 2,6-$i\mathrm{Pr_2C_6H_3}$) was reacted with $\mathrm{NaBAr^F{}_4}$ ($\mathrm{Ar^F}$ = 3,5-$\mathrm{(CF_3)_2C_6H_3}$) in the presence of allyl dimethyl amine (ADA) in diethyl ether solvent. This afforded the chelate complex $[\mathrm{(DAD)Pd(CH_2CHMeCH_2NMe_2)}][\mathrm{BAr^F{}_4}]$ (**1**, Scheme 1) in 52% isolated yield. The compound was characterized by single-crystal X-ray diffraction (Figure 1). It shows a five-membered chelate ring resulting from 1,2-insertion of the ADA olefinic moiety into the Pd−Me bond, although a certain amount of conformational disorder appears to be present in the chelate ring (judging from the relatively large thermal parameters; attempts to model this in this fragment were not successful). The Pd−N12 bond distance of the nitrogen atom that is *trans* to the chelate alkyl carbon is, at 2.215(4) Å, noticeably longer than the one *trans* to the amine donor (Pd−N11 = 2.078(4) Å). The room-temperature NMR spectra of **1** in $\mathrm{CD_2Cl_2}$ solvent show a fully asymmetric structure, with two diastereotopic methyl groups of the coordinated $\mathrm{NMe_2}$ moiety. The methyl group formerly bound to Pd shows a characteristic upfield ^{1}H

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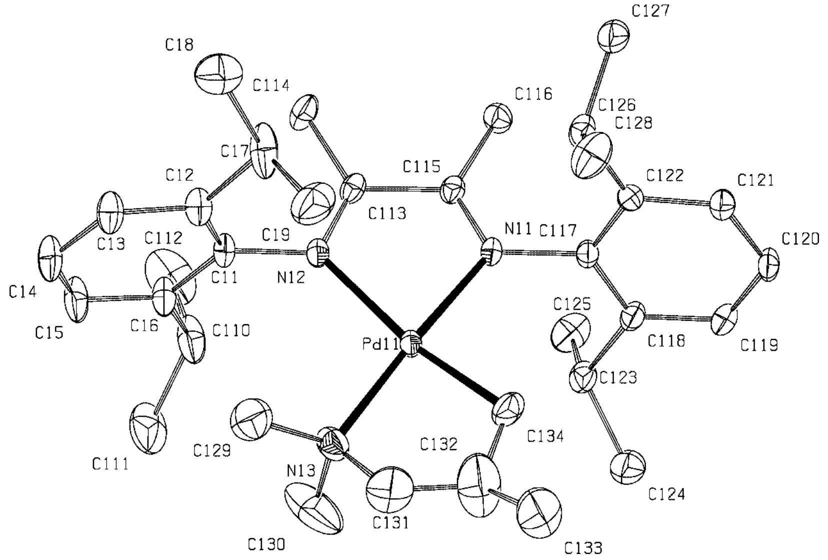


Figure 1. Molecular structure of [(DAD)Pd($CH_2CHMeCH_2NMe_2$)][BAr^F_4] (**1**). Thermal ellipsoids are at the 50% probability level. Selected bond distances (Å) and angles (deg): Pd11−N11 = 2.078(4), Pd11−N12 = 2.152(4), Pd11−N13 = 2.091(5), Pd11−C134 = 2.023(6), N11−Pd11−N12 = 76.67(15), N13−Pd11−C134 = 82.2(2).

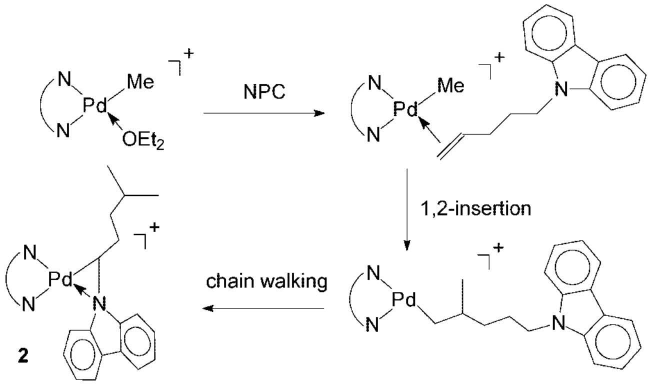
NMR shift at δ 0.67 ppm (d, $J = 6.8$ Hz). A reaction between the cationic Pd−Me species [(DAD)PdMe(OEt_2)][BAr^F_4][5] and ADA in CD_2Cl_2 monitored by ^1H NMR showed clean formation of **1**. Monitoring the reaction at low temperature (gradually warming from −60 °C) did not reveal any identifiable intermediates in the reaction.

Unlike the chelate complexes derived from the ether-functionalized olefins allyl ethyl ether and acrolein dimethyl acetal reported earlier,[4] the ADA chelate complex **1** does not effect the homopolymerization of ethylene under standard conditions (CH_2Cl_2 solvent, ambient temperature, 5 bar ethylene). Thus the increased donor strength of the trialkyl amine versus the ether renders the five-membered chelate too stable to allow interaction with and subsequent insertion of ethylene. Consistently, attempts to copolymerize ethylene with ADA using either **1** or [(DAD)PdMe(OEt_2)][BAr^F_4] as catalyst afforded no polymer.

Reaction with *N*-Pentenylcarbazole (NPC). Reaction of [(DAD)PdMe(OEt_2)][BAr^F_4] with *N*-pentenylcarbazole (NPC) in dichloromethane solvent at ambient temperature, followed by layering with pentane, afforded red crystals of the 1:1 reaction product [(DAD)Pd(η^2-$Me_2CHCH_2CH_2CHNC_{12}H_8$)][$BAr^F_4$] (**2**, Scheme 2) in 55% isolated yield. A crystal structure determination of **2** (Figure 2) revealed a three-membered chelate structure in which the carbazole nitrogen is coordinated to Pd and where the carbon atom in the chelate ring bears a 3-methylbut-1-yl substituent. The chelate ring is essentially coplanar with the (DAD)Pd ring, with a dihedral angle C141−Pd1−N11−C113 of 178.4(4)°. The carbazole nitrogen atom deviates only a little from planarity (sum of the three C−N−C angles is 351.9°).

The NMR spectra of **2** were fully assigned, including the connectivity in the 3-methylbut-1-yl substituent, using a combination of 1D and 2D (COSY, HSQC, HMBC) techniques. The CH group in the three-membered chelate shows resonances at δ 4.29 ppm (^1H, dd, $J = 5.7$ and 7.8 Hz) and 63.81 ppm (^{13}C, d, $J = 160$ Hz). When the reaction of [(DAD)PdMe(OEt_2)][BAr^F_4] with NPC in CD_2Cl_2 was monitored by NMR spectroscopy at temperatures from −65 °C upward, it was seen that at −50 °C the coordinated ether had completely been liberated and that full conversion to **2** (as only organometallic product) had already taken place, without any observable intermediates. This suggests that NPC initially coordinates to Pd through the olefinic moiety in what appears to be the rate-determining step, followed by rapid and selective 1,2-insertion into the Pd−Me bond. Rapid chain-walking[6] through β-H elimination, alkene rotation, and reinsertion then leads to the thermodynamically most favorable state, the three-membered chelate complex **2** (Scheme 2). In this complex, the steric interference between the carbazole moiety and the ligand substituents is minimized, and a favorable Pd−N interaction can be obtained without the need for significant pyramidalization of the carbazole nitrogen atom. Nevertheless, this three-membered chelate in **2** is substantially more reactive than the five-membered chelate in **1** and is readily able to initiate the catalytic homopolymerization of ethylene. In a typical experiment, using 1.8 μmol of **2** in 10 mL of CH_2Cl_2 at ambient temperature with 5 bar of ethylene pressure and 17.5 h run time, 1.42 g of branched polyethylene (45.5 kg(PE) mol^{-1} h^{-1}) was obtained ($M_w = 676\,500$ $M_w/M_n = 2.2$).

Scheme 2



Reaction with *N*-Allyl Carbazole (NAC). In a similar fashion as described above for NPC, the reaction of the cationic

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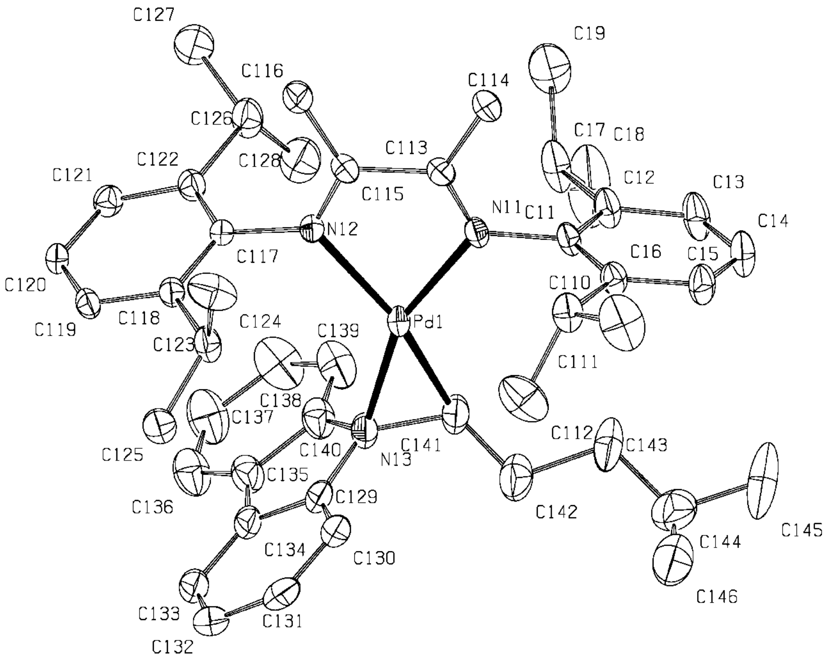
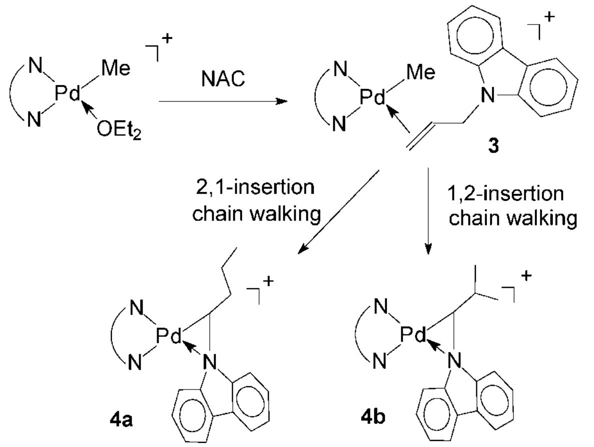


Figure 2. Molecular structure of [(DAD)Pd(η^2-$Me_2CHCH_2CH_2CHNC_{12}H_8$)][$BAr^F{}_4$] (**2**). Thermal ellipsoids are at the 50% probability level. Selected bond distances (Å) and angles (deg): Pd1−N11 = 2.085(3), Pd1−N12 = 2.143(4), Pd1−N13 = 2.104(5), Pd1−C141 = 2.015(7), N13−C129 = 1.453(7), N13−C140 = 1.450(8), N13−C141 = 1.449(8), N11−Pd1−N12 = 75.32(14), N13−Pd1−C141 = 41.1(2).

Scheme 3



palladium methyl complex [(DAD)PdMe(OEt_2)][$BAr^F{}_4$] with *N*-allyl carbazole (NAC) in CD_2Cl_2 was studied by low-temperature NMR spectroscopy. After 5 min at −50 °C, the coordinated ether had been displaced by the substrate, but now the initial product appears to be the alkene complex [(DAD)PdMe(η^2-CH_2=$CHCH_2NC_{12}H_8$)][$BAr^F{}_4$] (**3**, Scheme 3). The ^1H NMR resonances of the olefinic part of bound NAC in **3** are found at δ 4.95 (m, =CH−), 4.58 (d, J = 14.6 Hz, =CH*H*), and 4.44 (m, =C*H*H), compared to δ 6.07, 5.22 (d, J = 10.3 Hz), and 5.08 (d, J = 17.1 Hz), respectively, for free NAC. The Pd−Me ^1H resonance is a singlet at δ 0.47 ppm, showing that no olefin insertion has taken place yet. At −50 °C a slow sequential reaction can be observed. Warming to 0 °C takes this to completion and reveals the formation of two products in approximately equal amounts. They appear to be the three-membered chelate complexes [(DAD)Pd(η^2-$RCHNC_{12}H_8$)]-[$BAr^F{}_4$] (R = *n*Pr, **4a**; R = *i*Pr, **4b**; Scheme 3), related to **2**, but differing in the substituent on the chelate carbon atom. Like **2**, product **4b** arises from 1,2-insertion of the olefin into the Pd−Me bond, leading via chain-walking to the three-membered chelate with an *i*Pr substituent. Product **4a**, with the *n*Pr substituent, derives from initial 2,1-insertion of the olefin. The observations suggest that the shorter spacer between the olefinic and carbazole moieties in NAC, compared to NPC, increases the barrier to insertion into the Pd−Me bond (allowing the olefin complex to be observed for NAC, which was not the case for NPC under the same conditions) and erases the kinetic preference for 1,2- versus 2,1-insertion that is displayed by NPC.

Copolymerization of Ethylene with Carbazole-Containing Monomers. The copolymerization of ethylene with the carbazole-containing comonomers NPC and NAC was investigated using the ADMA chelate complex {(DAD)Pd($CH_2CHMeCH(OMe)_2$)}[$BAr^F{}_4$] (**5**)[4] as the introduced catalyst species. In Table 1 the results are depicted for ethylene/NPC copolymerization at ambient temperature in dichloromethane solvent. As can be seen from the first three entries, the addition of NPC substrate in various concentrations has no detrimental effect on the catalyst productivity. With increasing NPC concentration an increasing amount of NPC is incorporated into the polymer. The highest NPC incorporation (18 wt %) was obtained from an experiment at lower ethylene pressure (2 bar). NMR spectroscopy shows that these poly(ethylene-*co*-NPC) copolymer samples are branched polyethylenes containing incorporated carbazole functionalities and that they are free of unreacted monomer. The ^1H NMR spectrum of the copolymer containing 18 wt % NPC is shown in Figure 3. It indicates that essentially all carbazole groups in the copolymer have at least two methylene groups between the carbazole nitrogen and the rest of the polymer chain: the resonances for the α-CH_2 group (δ 4.25 ppm) and the β-CH_2 group (δ 1.85 ppm) have intensities that are equal to that of the carbazole 4,5-protons (δ 8.10 ppm). This implies that the carbazole functions are not incorporated into the polymer via direct ethylene insertion into a three-membered chelate species like **2**, as this would create a secondary carbon adjacent to the carbazole nitrogen atom. Thus, either the chain-walking process after NPC insertion is slower than the capture of a new ethylene

Table 1. Copolymerization of Ethylene with NPC Using ADMA-Chelate Complex 5 as Catalyst

conditions[a]	NPC (mmol)	polymer yield (g)	productivity[b] (kg mol^{-1} h^{-1})	M_w ($\times 10^{-3}$)	M_w/M_n	NPC content (wt %)[b]
A	0	3.50	13.0	186	1.5	0.0
A	2.1	3.50	13.0	350	1.7	1.6
A	3.8	4.03	15.0	259	1.6	5.0
B	6.0	0.63	11.8	279	3.4	18.8

[a] A: 13.4 μmol of **5**, 15 mL of CH_2Cl_2, 5 bar of ethene, room temperature, 20 h run time; B: 13.4 μmol of **5**, 15 mL of CH_2Cl_2, 2 bar of ethene, room temperature, 4 h run time. [b] Note that the productivities appear relatively low due to the high catalyst concentration and long reaction times employed to maximize the absolute polymer yield.

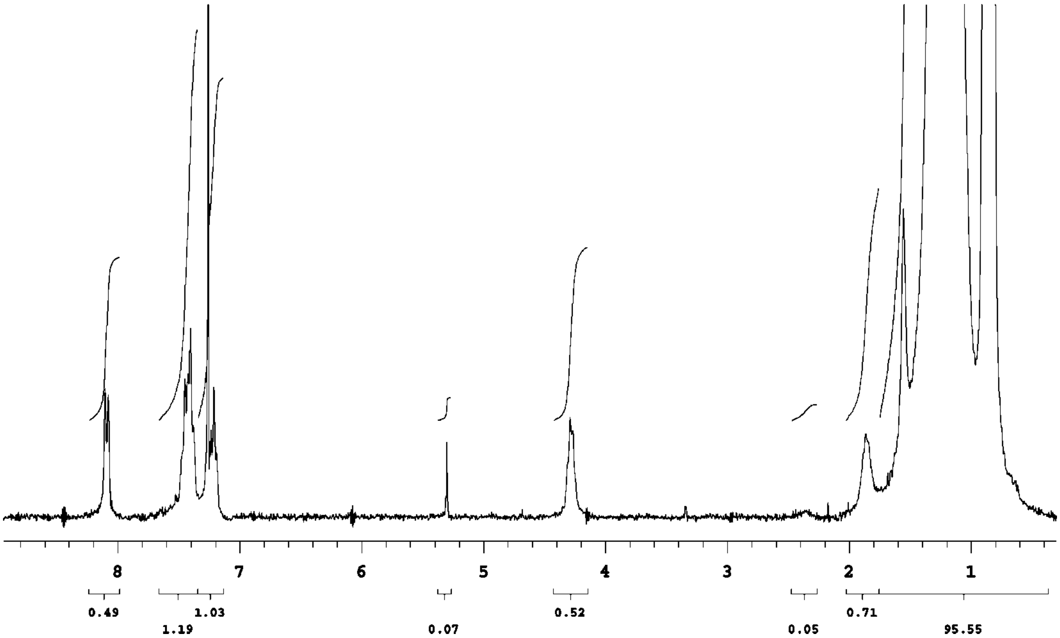


Figure 3. ^1H NMR spectrum ($CDCl_3$, 23 °C, 300 MHz) of a branched ethylene-NPC copolymer with 18.8 wt % NPC incorporated.

molecule, or chain-walking is fast and can occur to, as well as from, the three-membered chelate (in the latter case enabling ethene capture and insertion). In view of available data on (co)polymerization with Pd α-diimine catalysts, the latter option is deemed more likely.

In contrast with the above results with NPC, analogous copolymerization experiments with NAC afforded only branched polyethylene homopolymer, even under more forcing conditions (an experiment at 50 °C, 1.1 M NAC in dichloromethane, 5 bar of ethylene after 1.5 h afforded 3.0 g of branched polyethylene homopolymer at 59.6 kg(PE) mol^{-1} h^{-1}). From the reactions of $[(DAD)PdMe(OEt_2)][BAr^F_4]$ with NAC and NPC, described above, it appears that the barrier to insertion into the Pd−alkyl bond is substantially higher for NAC than for NPC. Apparently, under the applied conditions, NAC either cannot compete with ethylene for the binding to the Pd center or, when coordinated to the metal, is too slow to insert into the Pd−alkyl bond to prevent its rapid displacement from the metal center by incoming ethylene.

The carbazole group is known to exhibit aggregation-dependent fluorescence behavior. Isolated *N*-alkylated carbazole groups show fluorescence around 365 nm, but carbazole groups that are closely associated show fluorescence at longer wavelengths ("monomer" versus "excimer" fluorescence).[7] The amorphous ethene/NPC copolymers exhibit visible fluorescence under UV irradiation. Two of these copolymers, with 5.0 wt % and 18.8 wt % NPC contents, were studied by emission fluorescence spectrometry. For the copolymer with low NPC content (5.0 wt %), mainly the locally excited state of the carbazole chromophore at 365 nm was observed (Figure 4, top). But for the copolymer with higher NPC content (18.8 wt%), a significantly increased emission intensity is seen around 410 nm (Figure 4, bottom). As the copolymers produced with this catalyst are amorphous, the carbazole groups are essentially distributed evenly over the volume of the polymer. The ratio of monomer versus excimer fluorescence decreases with increasing NPC content of the copolymer.

Experimental Section

General Procedures. All experiments were carried out under an atmosphere of purified nitrogen using standard Schlenk and glovebox techniques, unless mentioned otherwise. CH_2Cl_2 and CD_2Cl_2 (Aldrich) were distilled from CaH_2 prior to use. Ether, toluene, and pentane (Aldrich, anhydrous, 99.8%) were dried by passing over columns of Al_2O_3, BASF R3-11 supported Cu oxygen scavenger, and molecular sieves (Aldrich, 4 Å) under a nitrogen atmosphere prior to use. NMR spectra were recorded on Varian Gemini 300/500 spectrometers in NMR tubes equipped with a Teflon (Young) valve. The ^1H NMR spectra were referenced to resonances of residual protons in the deuterated solvents, δ 5.32 ppm for CD_2Cl_2. The ^{13}C NMR spectra were referenced to the carbon resonances of the deuterated solvents, δ 53.8 ppm for CD_2Cl_2. Chemical shifts are given relative to tetramethylsilane (downfield shifts are positive); *J* values are given in hertz. Assignments of the resonances of the organometallic products were

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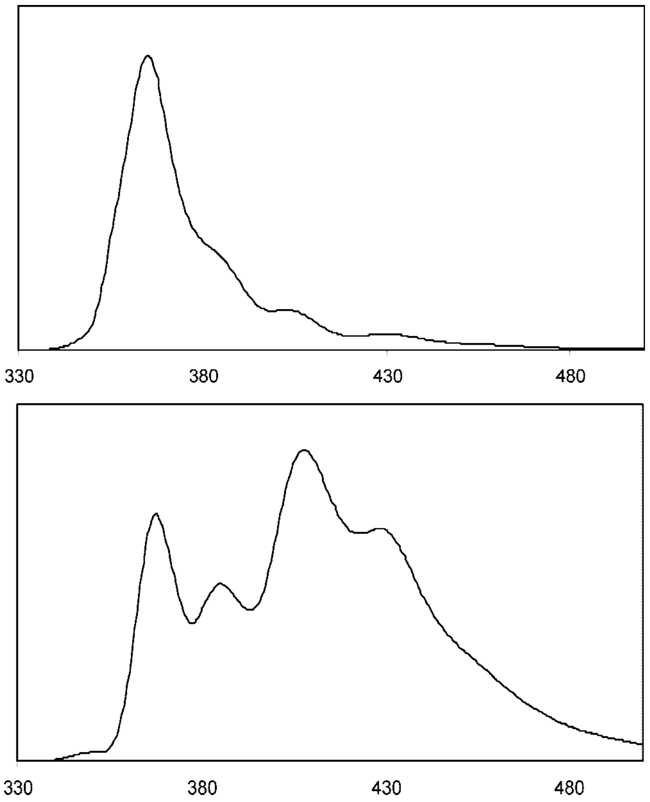

Figure 4. Emission fluorescence spectrum of branched ethylene-NPC copolymers with 5.0 wt % (top) and 18.8 wt % (bottom) NPC incorporated. Horizontal scale: λ (nm), vertical scale: au. Excitation wavelength: 295 nm.

made using information from COSY and HSQC (heteronuclear single quantum coherence) and/or HMBC (heteronuclear multiple bond coherence) spectra. GPC analysis of the polymers was performed at ambient temperature on a Spectra Physics AS 1000 LC-system using a Viscotek H-502 viscometer and a Shodex RI-71 refractive index detector, using THF as eluent and universal calibration with polystyrene standards. Emission fluorescence spectra were recorded on a Perkin-Elmer LS 50B instrument from a pressed solid sample of 13 mm diameter and 2 mm thickness at ambient temperature. The excitation wavelength was 295 nm, with excitation and emission widths of 10 nm and a scan rate of 100 nm/min. The compounds (DAD)PdMeCl (DAD = ArN=CMe−CMe=NAr, Ar = 2,6-$i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3$),[5] $\mathrm{NaBAr^F}_4$ ($\mathrm{Ar^F}$ = 3,5-$(\mathrm{CF}_3)_2\mathrm{C}_6\mathrm{H}_3$),[8] and $\{\mathrm{(DAD)Pd(CH_2CHMeCH(OMe)_2}\}[\mathrm{BAr^F}_4]$[4] were prepared according to published procedures. $\mathrm{NaBAr^F}_4$ was dried at 130 °C under vacuum for 6 h. $[\mathrm{(DAD)PdMe(OEt_2)}][\mathrm{BAr^F}_4]$ was prepared using a slightly modified version of the published procedure.[5] *N*-Pentenylcarbazole (NPC) and *N*-allylcarbazole (NAC) were synthesized from carbazole, NaH, and 5-bromopentene-1 or allyl bromide following the procedure described by Kim et al.[9] Allyl dimethyl amine (ADA, Acros 98%) was used as received. Elemental analyses were performed by Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

NMR Data for $[\mathrm{BAr^F}_4]^-$ Anion. The ^{1}H and ^{13}C NMR resonances of $[\mathrm{BAr^F}_4]^-$ anion in $\mathrm{CD_2Cl_2}$ are the same in the spectra for the different cationic palladium complexes at various temperatures. They are give here and will not be repeated in the listing of the other spectra. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 500 MHz, 25 °C): δ 7.73 (s, 8H, H_o), 7.57 (s, 4H, H_p). ^{13}C NMR ($\mathrm{CD_2Cl_2}$, 126 MHz, 25 °C): δ 162.13 (q, J_{CB} = 50.6, $\mathrm{C_{ipso}}$), 135.20 (C_o), 129.31 (qq, J_{CF} = 31.5, J_{CB} = 2.9, C_m), 124.99 (q, J_{CF} = 273.1, $\mathrm{CF_3}$), 117.83 (septet, J_{CF} = 3.9, C_p).

NMR Tube Scale Reactions of $[\mathrm{(DAD)PdMe(Et_2O)}][\mathrm{BAr^F}_4]$ with Functionalized Olefins. The α-diimine palladium complex $[\mathrm{(DAD)PdMe(EtO)_2}][\mathrm{BAr^F}_4]$ (about 0.02 mmol) was weighed into an NMR tube in a drybox under $\mathrm{N_2}$ atmosphere. The tube was then capped with a latex septum and taken out of the drybox. Solutions of monomers (1 equiv) in $\mathrm{CD_2Cl_2}$ (0.7 mL) were injected by syringe into the NMR tube that was cooled at −196 °C by liquid $\mathrm{N_2}$. Upon thawing out, the tube was shaken briefly to dissolve the palladium complex and transferred to the precooled probe of the NMR spectrometer. Spectra were acquired at regular temperature intervals.

Reaction of $[\mathrm{(DAD)PdMe(Et_2O)}][\mathrm{BAr^F}_4]$ with *N*-Allylcarbazole. After 5 min at −50 °C, the coordinated ether had been displaced by the olefinic moiety of the substrate, yielding the olefin complex **3**. Incipient insertion of NAC into the Pd−Me bond (producing the three-membered chelate complexes **4a** and **4b**) was already observed at this temperature. Upon increasing the temperature, the insertion reaction progressed, until at 0 °C all of **3** had disappeared. The ratio of the three-membered chelate complexes **4a** and **4b** at all stages of the reaction was about 1:1. The assignments of the NMR spectra of **4a** and **4b** are supported by 2D NMR (COSY), but DAD ligand resonances could not be assigned due to extensive overlap in the mixture. $\{\mathrm{(DAD)Pd(Me)}[\eta^2\mathrm{CH_2{=}CHCH_2N(C_6H_4)_2}]\}[\mathrm{BAr^F}_4]$ (**3**): ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 500 MHz, −55 °C) δ 8.06 (d, J = 7.8, $\mathrm{N(C_6H_3}H)_2$), 4.95 (m, CHH′=C*H*), 4.58 (d, J = 14.6, C*H*H′=CH), 4.44 (m, CH*H′*=CH), 4.27 (d, 2H, J = 8.4, $\mathrm{C}H_2\mathrm{N(C_6H_4)_2}$), 2.41 and 2.24 (s, 3H each, N=C*Me*), 0.47 (s, 3H, Pd*Me*). $\{\mathrm{(DAD)Pd[MeCH_2CH_2CHN(C_6H_4)_2]}\}[\mathrm{BAr^F}_4]$ (**4a**): ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 500 MHz, 25 °C) δ 4.32 (t, J = 6.4, PdC*H*), 1.48 (m, 2H, $\mathrm{MeCH_2C}H_2$), 1.08 (m, 2H, $\mathrm{MeC}H_2$), 0.46 (t, 3H, J = 6.8, $Me\mathrm{CH_2}$). $\{\mathrm{(DAD)Pd[Me_2CHCHN(C_6H_4)_2]}\}[\mathrm{BAr^F}_4]$ (**4b**): ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 500 MHz, 25 °C) δ 4.18 (d, J = 10.9, PdC*H*), 2.33 (m, $\mathrm{Me_2C}H$), 0.25 and 0.11 (d, 3H each, J = 6.4, $Me_2\mathrm{CH}$).

Synthesis of $[\mathrm{(DAD)Pd(CH_2CHMeCH_2NMe_2)}][\mathrm{BAr^F}_4]$ (1). Allyl dimethyl amine (0.1 mL, 1.6 mmol) was added to a solution of (DAD)PdMeCl (157 mg, 0.29 mmol) and $\mathrm{Na[BAr^F}_4]$ (210 mg, 0.24 mmol) in 20 mL of $\mathrm{Et_2O}$. The mixture was stirred at 20 °C for 3 days. After filtration, the solvent was evaporated under vacuum. The orange solid was washed with pentane (10 mL) three times, affording compound **1** (225 mg, 0.15 mmol, 52%). ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 500 MHz, 25 °C): δ 7.44–7.30 (m, 6H, $\mathrm{H_{aryl}}$), 3.00 and 2.88 (m, 4H, *i*Pr C*H*), 2.41 (s, 3H, N*Me*Me′), 2.28 (m, 2H, $\mathrm{C}H_2\mathrm{N}$), 2.21 and 2.13 (s, 3H each, N=C*Me*), 1.91 (m, C*H*), 1.88 (s, 3H, NMe*Me′*), 1.75 (dd, J = 8.8, J' = 11.4, PdC*H*H’), 1.41 and 1.28–1.10 (m, 24H, *i*Pr *Me*), 1.24 (PdCH*H′*), 0.67 (d, 3H, J = 6.8, CH*Me*). ^{13}C NMR ($\mathrm{CD_2Cl_2}$, 126 MHz, 25 °C): δ 178.9 and 173.41 (N=*C*Me), 142.53 and 141.87 (Ar $\mathrm{C_{ipso}}$), 138.27, 137.99, 137.87, and 137.61 (Ar C_o), 129.01 and 128.89 (Ar C_p), 125.53, 125.34, 124.91, and 124.84 (Ar C_m), 76.03 (t, J_{CH} = 123, $C\mathrm{H_2N}$), 52.51 (q, J_{CH} = 138, NMe), 49.65 (q, J_{CH} = 138, NMe), 43.66 (t, J_{CH} = 129, $\mathrm{Pd}C\mathrm{H_2}$), 35.61 (d, J_{CH} = 122, *C*H), 29.41, 29.22, 29.12, and 29.08 (*i*Pr *C*H), 23.0 and 21.70 (N=C*Me*), 15.50 (q, J_{CH} = 129, $Me\mathrm{CH_2}$). Anal. Calcd for $\mathrm{C_{70}H_{76}N_3BF_{24}Pd}$: C, 53.76; H, 4.51; N, 2.85. Found: C, 53.4; H, 4.3; N, 2.9.

Synthesis of $\{\mathrm{(DAD)Pd[Me_2CHC_2H_4CHN(C_6H_4)_2]}\}[\mathrm{BAr^F}_4]$ (2). *N*-Pentenylcarbazole (13.6 mg, 0.06 mmol) was added to a solution of $[\mathrm{(DAD)PdMe(EtO)_2}][\mathrm{BAr^F}_4]$ (84.6 mg, 0.06 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL). The solution was stirred at 20 °C overnight. After addition of pentane (50 mL) the solution was kept at 20 °C for 2 days. Dark red crystals (53 mg, 0.033 mmol, 55%) of **2** were isolated. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 500 MHz, 25 °C): δ 7.79, 7.64, 6.99, 6.89, and 6.86 (t, d, t, d, d, 1H each, J = 7.5–7.9, carb), 7.5−7.3 (m, 9H, $\mathrm{H_{aryl}}$ and carb), 4.29 (dd, J = 5.7, J' = 7.8, PdC*H*), 3.59, 2.94, 2.69, and 2.56 (septet, 1H each, J = 6.8, *i*Pr C*H*), 2.24 and 2.04 (s, 3H each, N=C*Me*), 1.65, 1.64, 1.33, 1.30, 1.02, 0.99, 0.88, and 0.48 (d, 3H

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each, *i*Pr *Me*), 1.5 (overlapping, $\mathrm{CH}\mathit{H}\mathrm{CHPd}$ and $\mathrm{Me_2C}\mathit{H}$), 1.1 ($\mathrm{CH}\mathit{H}\mathrm{CHMe_2}$), 1.0 ($\mathit{C}\mathrm{HHCHPd}$), 0.53 and 0.52 (d, 3H each, J = 8.3, $\mathit{Me}_2\mathrm{CH}$), 0.48 ($\mathit{C}\mathrm{HHCHMe_2}$). ^{13}C NMR ($CD_2Cl_2$, 126 MHz, 25 °C): δ 175.55 and 172.04 ($\mathrm{N{=}}\mathit{C}\mathrm{Me}$), 146.63, 144.47, 135.18, 132.22, 129.07, 127.66, 125.44, 124.02, 121.35, 117.85, 113.68, and 99.89 (Ar: carbazole), 143.18 and 142.72 (Ar C_{ipso}), 139.34, 138.05, 137.14, and 136.96 (Ar C_o), 129.07 and 128.39 (Ar C_p), 128.07, 127.51, 125.23, and 124.9 (Ar C_m), 63.81 (d, J_{CH} = 160, $\mathrm{Pd}\mathit{C}\mathrm{H}$), 35.98 (t, J_{CH} = 124, $\mathit{C}\mathrm{H_2CHMe_2}$), 30.29, 29.80, 29.37, and 29.29 (*i*Pr *C*H), 28.55 (*t*, J_{CH} = 146.6, $\mathit{C}\mathrm{H_2CHPd}$), 23.16 and 21.83 (q, J_{CH} = 123, $\mathit{Me}_2\mathrm{CH}$), 24.59–21.83 (8C, *i*Pr *Me*), 20.69 and 20.04 (q, J_{CH} = 127, $\mathrm{N{=}C}\mathit{Me}$). Anal. Calcd for ($C_{78}H_{72}N_3BF_{24}Pd$): C, 57.67; H, 4.47; N, 2.59. Found: C, 57.62; H, 4.42; N, 2.71.

Catalytic Polymerization Experiments. The homo- and copolymerizations were performed in a 50 mL glass miniclave (Büchi AG, Switzerland) with a Teflon-coated magnetic stirrer. Before use, the reactor was dried at 80 °C in a vacuum oven for 2 h. A typical reaction procedure was as follows: In a nitrogen-filled glovebox, the miniclave was charged sequentially with (1) Pd catalyst, (2) the desired amount of comonomers (for copolymerizations), and (3) dichloromethane. The reactor was closed, taken out of the glovebox, put on a magnetic stirrer at room temperature, and pressurized with ethene. The ethene pressure was kept constant during the reaction by replenishing flow. After the specified reaction time, the reactor was vented, and the (co)polymerization was terminated by the addition of excess methanol. Further workup was performed under aerobic conditions. After the reaction mixture was stirred at room temperature for 1 h, the volatiles were evaporated under vacuum at 40 °C and the residue was extracted with petroleum ether. Subsequently the polymer was precipitated with methanol and the viscous product was dried under vacuum at 80 °C overnight.

X-ray Crystallography. Crystals of **1** and **2** suitable for X-ray diffraction were obtained by recrystallization from CH_2Cl_2/pentane. Crystallographic data and details of the refinements are found in Table S-1. With inert-atmosphere handling techniques, suitable crystals were mounted on top of a glass fiber and aligned on a Bruker SMART APEX CCD diffractometer. Intensity data were corrected for Lorentz and polarization effects, scale variation, decay, and absorption: a multiscan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (SADABS),[10] and reduced to F_o^2. The structures were solved by Patterson methods, and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF.[11] The positional and anisotropic displacement parameters for the non-hydrogen atoms were refined. Final refinement on F^2 was carried out by full-matrix least-squares techniques.

Compound 1. Rotational disorder was present in several of the CF_3 groups of the anion, and some of them were refined using two alternative positions. The apparent displacement factors of the carbon atoms in the chelate C131−C134 also suggest some conformational disorder, but this could not be satisfactorily modeled.

Compound 2. Rotational disorder was present in several of the CF_3 groups of the anion, and some of them were refined using two alternative positions. Some conformational disorder may be present in the 3-methylbut-1-yl substituent C142−C146 as suggested by the relatively large displacement factors.

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Supporting Information Available: Spectral data for **2** and polymers. Crystallographic data for **1** and **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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