Inorganic Chemistry

ARTICLE

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Highly Active Titanium-Based Olefin Polymerization Catalysts Bearing Bulky Aminopyridinato Ligands

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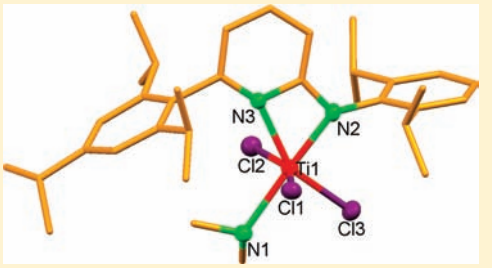
Supporting Information

ABSTRACT: A series of titanium complexes have been prepared using either salt metathesis or amine elimination reactions. Reacting the potassium salt of Ap*H {Ap*H = *N*-(2,6-diisopropylphenyl)-[6-(2,4,6-triisopropylphenyl)pyridin-2-yl]-amine} (**1**) with $[TiCl_4(THF)_2]$ results in the formation of a nucleophilic ring-opening product of the coordinated tetrahydrofuran (THF) ligand $[Ap^*TiCl_2(OC_4H_8Cl)]$ (**7**). Alkylation with benzylmagnesium chloride gave rise to the corresponding benzyl complex $[Ap^*TiBn_2(OC_4H_8Cl)]$ (**8**). However, THF ring opening was overcome by adopting an amine elimination route instead of salt metathesis. Mono(aminopyridinato)titanium trichloro complexes were prepared in high yields using $[(CH_3)_2NTiCl_3]$, together with the corresponding sterically demanding aminopyridine as the starting material. The synthesized complexes could then be alkylated selectively. These complexes were characterized by spectroscopic methods, and their behavior in olefin polymerization and copolymerization of ethene and propene was explored. These mono(aminopyridinato)titanium trichloro complexes are less active if activated with methylaluminoxane (MAO). However, the activity increases strongly if MAO is replaced by d-MAO ("dry methylaluminoxane"). The catalysts show moderate activity toward propene polymerization, while ethylene−propylene copolymers in high-productivity with separated propene units were observed. The catalysts are also highly active in the co- and terpolymerization of 2-ethylidenenorbornene (ENB) with ethylene or ethylene−propylene, together with a very good incorporation of ENB. In all cases, the activity increases with an increase in the steric bulk of the protecting ligand.

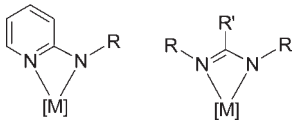


INTRODUCTION

Aminopyridinato ligands (Scheme 1, left) have been investigated intensively during the past decade.[1−3] They are monoanionic ligands suited to stabilizing early transition metals in high oxidation states. The ligand "asymmetry" caused by the two different donor functionalities, the pyridine and amido functions, might be considered as an additional interesting feature, especially in comparison to the closest "relatives", the amidinates (Scheme 1, right).[4]

Titanium aminopyridinates have been described especially with regard to olefin polymerization chemistry.[5] Recently, we started a research program involving very bulky aminopyridinato ligands.[6] A variety of these (non-titanium) complexes have proven to be efficient olefin polymerization catalysts. Hence, we became interested in exploring the olefin polymerization chemistry of titanium complexes stabilized by these bulky versions of aminopyridinato ligands. It has been observed in the past that the best way to synthesize aminopyridinatotitanium complexes is "direct synthesis" or amine elimination reactions.[5] Salt metathesis involving lithiated aminopyridines often leads to low yields.[5] To increase the yield, we used the potassium salt of the corresponding ligand. This has been shown to be an efficient alternative for the preparation of lanthanoid aminopyridinates, where lithiated aminopyridines were also unable to give the desired product.[6b] Unfortunately, we observed that the use of the potassium salt of aminopyridine led to ring opening of the coordinated tetrahydrofuran (THF), yielding an alkoxy species. Here, we report on the synthesis and structure of titanium complexes stabilized by bulky aminopyridinato ligands and their behavior in olefin homo-, co-, and terpolymerization. The production of EPDM (= ethylene, propylene, diene, and monomers) rubber by such catalyst systems will be discussed as well.

Scheme 1. Aminopyridinato (left) and Amidinate (right) Ligands ([M] = Group 4 Metal Complex Moiety; R, R′ = Substituents)



RESULTS AND DISCUSSION

Synthesis and Structures of Complexes. The aminopyridines **1**−**4** (Scheme 2) can be synthesized according to published procedures.[6a,d,7]

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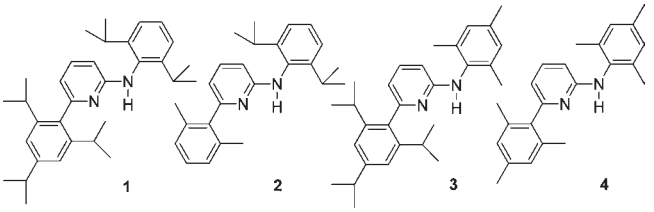
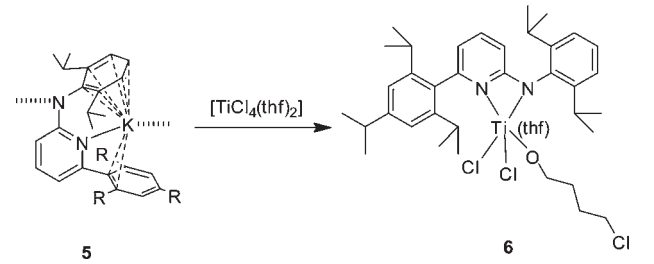
Scheme 2. Applied Aminopyridines



Scheme 3. Synthesis of 6 (R = Isopropyl)



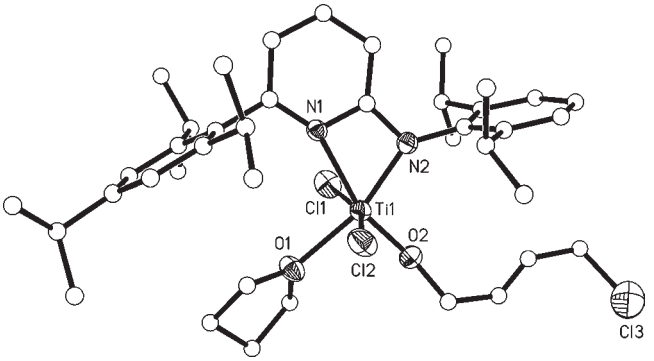
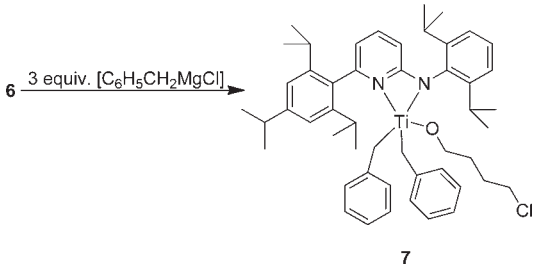


Figure 1. Molecular structure of **6**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: N1−Ti1 2.269(3), N2−Ti1 1.972(3), Cl1−Ti1 2.3472(12), Cl2−Ti1 2.3349(12), Ti1−O2 1.741(3), Ti1−O1 2.173(3); O2−Ti1−O1 95.60(11), N2−Ti1−O1 164.88(11), O2−Ti1−N1 162.11(12), N2−Ti1−N1 62.71(10), Cl2−Ti1−Cl1 160.32(5).

The reaction of 1 equiv of the potassium salt of **1**[6a] in THF with $[TiCl_4(THF)_2]$ and crystallization from hexane at low temperature lead to the formation of THF ring-opening product **6**, in very good yield (Scheme 3).

Such kind of behavior appears reasonable and has been explained as being the result of a nucleophilic THF ring-opening reaction through nucleophilic attack by the free Cl^- on the activated C−O bond of the coordinated THF.[8] This process would give rise to complex **6**. Previous examples of this type of reactivity between the $[Cp_2Zr(R)(THF)]^+$ species and certain nucleophilic reagents, namely, NR_3 and PMe_2Ph, have been described by Jordan et al.[9] Furthermore, nucleophilic attack of a chloride anion on a coordinated THF molecule has been previously observed in other instances where THF is bound to an electrophilic center, namely, boron and uranium.[10] Recently, such a nucleophilic THF ring opening has been reported for yttrium β-diketiminate complexes.[11]

Scheme 4. Synthesis of 7



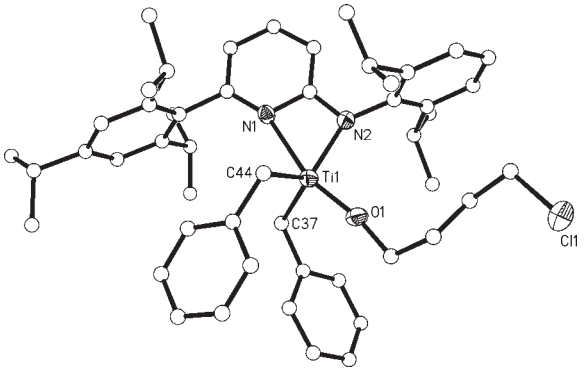
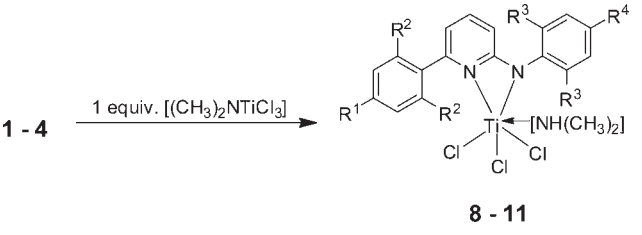


Figure 2. Molecular structure of **7**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ti1−O1 1.745(3), Ti1−N2 1.989(4), Ti1−C37 2.113(4), Ti1−C44 2.122(5), Ti1−N1 2.338(3); O1−Ti1−C37 99.96(16), N2−Ti1−C37 116.89(17), O1−Ti1−C44 98.35(17), C37−Ti1−C44 115.6(2), O1−Ti1−N1 163.02(14), N2−Ti1−N1 61.48(13), C37−Ti1−N1 88.83(15), C44−Ti1−N1 90.76(15).

Scheme 5. Synthesis of 8 ($R^1 = R^2 = R^3 = i$-Pr, R^4 = H), 9 ($R^1 = R^4$ = H, R^2 = Me, $R^3 = i$-Pr), 10 ($R^1 = R^2 = i$-Pr, $R^3 = R^4$ = Me), and 11 ($R^1 = R^2 = R^3 = R^4$ = Me)



Complex **6** can be crystallized from a concentrated hexane solution as dark-red crystals. The coordination sphere around the titanium atom is pseudooctahedral (Figure 1), with two chlorides [Cl2−Ti1−Cl1 160.32(5)°] in the trans position to each other. The coordination sphere consists of two nitrogen atoms, two oxygen atoms, and two chloride atoms, and the reason for the distortion is the small angle of the aminopyridinato four-membered ring [N2−Ti1−N1 62.71(10)°]. In an attempt to get rid of the alkoxy ligand and to synthesize the trialkyl complex, 3 equiv of benzylmagnesium chloride was reacted with **6** in ether at room temperature. Compound **7** was formed in very good yield (Scheme 4).

Crystals of **7** partially suitable (the quality of the diffraction data is rather low) for X-ray analysis were obtained from pentane.

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The coordination around the metal center can best be described as distorted trigonal bipyramidal (Figure 2). Again, the reason for the distortion is the small N−Ti−N bond angle [61.48(13)°] due to strained binding of the aminopyridinato ligand. The different Ti−N distances of **6** [Ti−N1 2.269(3) Å; Ti−N2 1.972(3) Å] and **7** [Ti−N1 2.338(3) Å; Ti−N2 1.989(4) Å] indicate localization of the anionic function at the amido nitrogen atom. The ^{1}H NMR spectrum of **7** shows a pentate and two triplets at 1.01 (4H, H^{2CH_2}), 2.88 (2H, H^{CH_2Cl}), and 3.59 (2H, H^{OCH_2}) ppm, respectively, for the opened THF ring. The two nonequivalent CH_2 protons of the benzyl ligands gave rise to two doublets (AB system) at 2.71 and 2.82 ppm.

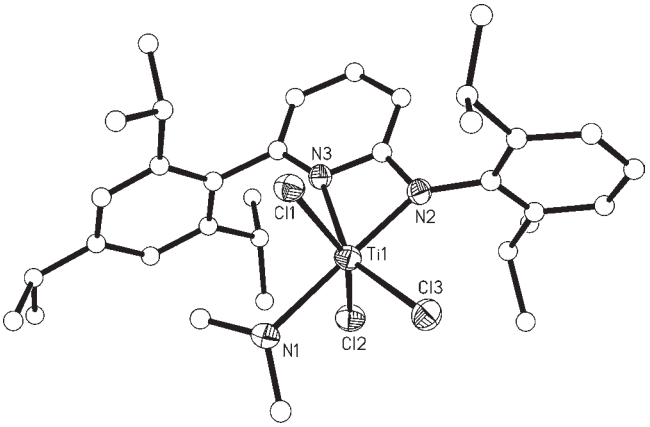
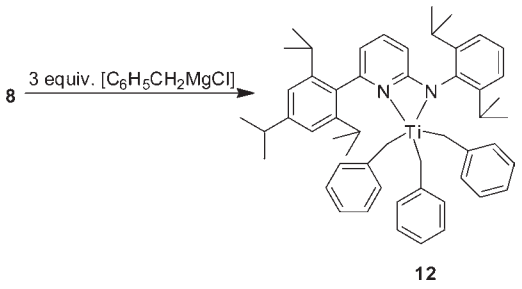


Figure 3. Molecular structure of **8**. Hydrogen atoms and one molecule are omitted for clarity. Selected bond lengths [Å] and angles [deg]: N1−Ti1 2.261(5), N2−Ti1 1.981(4), N3−Ti1 2.233(5), Cl1−Ti1 2.3269(18), Cl2−Ti1 2.2857(18), Cl3−Ti1 2.2430(16); N2−Ti1−N3 63.05(16), N2−Ti1−Cl3 88.95(13), N3−Ti1−Cl3 151.99(13), N3−Ti1−N1 118.72(15), Cl3−Ti1−Cl2 102.55(7), Cl3−Ti1−Cl1 99.94(6), Cl2−Ti1−Cl1 152.65(7).

Scheme 6. Synthesis of 12



Compounds **8** and **11** were crystallized as purple crystals from a concentrated ether solution at low temperature. X-ray crystal structures were determined for both compounds. The molecular structure of compound **8** is shown in Figure 3. Both compounds adopt a distorted octahedral coordination due to the additional dimethylamine ligand, which was released during the amine elimination reaction.

To explore the nature of coordinated amine and its possible role in the aminopyridinatotitanium-catalyzed olefin polymerization reactions, alkylation of complex **8** was modeled. The reaction of **8** with benzylmagnesium chloride in diethyl ether yielded the amine-free trialkyl **12** (Scheme 6).

After removal of all volatiles and extraction of the residue with hexane, the ^{1}H NMR spectrum of the red crystalline material obtained at low temperature shows that all of the benzyl protons in **12** are equal. The CH_2-group resonance of these ligands was observed as a single sharp signal at 3.10 ppm. No resonances related to dimethylamine could be detected. The tribenzyltitanium complex was not stable in solution at room temperature, leading to toluene

Table 1. Details of the X-ray Crystal Structure Analyses

	6	7	8	11
formula	$C_{40}H_{59}Cl_3N_2O_2Ti$	$C_{50}H_{65}ClN_2OTi$	$C_{25}H_{32}Cl_3N_3Ti$	$C_{34}H_{50}Cl_3N_3Ti$
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic
space group	*Pccn*	*P*21/*c*	*Cc*	*P*21/*c*
a [Å]	19.6630(10)	11.0340(10)	29.6950(6)	13.1900(12)
b [Å]	27.6460(11)	20.3610(10)	12.9390(4)	12.1140(10)
c [Å]	15.2850(6)	20.4070(10)	18.5580(5)	16.4750(14)
β [deg]		96.583(8)	91.387(2)	92.589(7)
V [Å^3]	8309.0(6)	4554.5(5)	7128.3(3)	2629.7(4)
cryst size [mm^3]	0.69 × 0.54 × 0.35	0.8 × 0.4 × 0.3	0.24 × 0.21 × 0.13	0.29 × 0.13 × 0.12
ρ_{calcd} [g cm^{-3}]	1.206	1.157	1.221	1.336
μ(Mo Kα) [mm^{-1}]	0.433	0.283	0.491	0.648
T [K]	133(2)	133(2)	133(2)	191(2)
θ range [deg]	1.27−25.79	1.42−25.76	1.37−25.65	1.55−25.71
no. of unique reflns	7891	8590	6779	4971
no. of obsd reflns [$I > 2\sigma(I)$]	5211	5653	4502	2816
no. of param	433	496	771	298
wR2 (all data)	0.177	0.200	0.070	0.117
R value [$I > 2\sigma(I)$]	0.064	0.081	0.033	0.062

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Table 2. Ethylene Polymerization Catalyzed by 6 and 8−11

entry	precatalyst[a]	MAO [mmol]	d-MAO [mmol]	T [°C]	$m_{Pol.}$ [g]	activity [$kg_{PE}\ mol_{cat}^{-1}\ h^{-1}\ bar^{-1}$]	M_w [g mol^{-1}]	M_w/M_n
1	**8**	1		50	1.20	480	66 162	2.3
2	**8**	1		80	0.30	120	55 267	2.3
3	**8**		1	30	7.10	2840	93 686	2.5
4	**8**		1	50	4.90	1960	85 109	2.6
5	**8**		1	80	4.80	1920	95 602	3.1
8	**9**		1	50	3.30	1320	67 190	2.3
6	**10**		1	50	2.40	960	89 093	2.7
7	**11**		1	50	2.20	880	63 716	2.9
9	**6**		1	50	2.00	800	45 507	5.5
10	**6**		1	80	4.70	1880	172 177	3.3

[a] Precatalyst: 2 μmol. Toluene: 260 mL. p = 5 bar. t = 15 min.

Table 3. Ethylene Copolymerization Catalyzed by 6 and 8−11

		pressure [bar]						
entry	precatalyst[a]	ethene	propene	T [°C]	$m_{Pol.}$ [g]	activity [$kg_{PE}\ mol_{cat}^{-1}\ h^{-1}$]	M_w [g mol^{-1}]	M_w/M_n
1	**8**		5	50	3.1	200	nd	nd
2	**8**	5	2	50	16.00	32 000	104 374	2.1
3	**9**	5	2	50	14.80	29 600	103 502	2.0
4	**10**	5	2	50	15.30	30 600	120 954	2.1
5	**11**	5	2	50	7.30	14 600	87 162	1,9
6	**6**	5	2	50	6.70	2 680	186 796	2.1
7[b]	**8**	5		50	16.50	33 000	133 287	2.4
8[c]	**8**	5		50	5.7	11 400		
9[d]	**8**	5	2	50	4.00	8 000	56 261	1.9

[a] Precat: 2 μmol. Toluene: 260 mL. d-MAO = 1 mmol. t = 15 min. [b] 10 mL of 1-hexene. [c] 10 mL of ENB. [d] 1 mL of ENB.

elimination and the formation of unidentified species, while at low temperature, it could be stored for weeks.

POLYMERIZATION STUDIES

Because the aim of this work was to evaluate the potential of titanium complexes stabilized by bulky Ap ligands in olefin polymerization, the use of these complexes in ethylene homo- and copolymerization was examined. Activation of **8** with MAO leads to an active single-site catalyst at 50 °C but shifted to moderate with an increase in the temperature to 80 °C (Table 2, entries 1 and 2). Because of possible decomposition and ligand transfer from titanium to aluminum,[6i,p] we switched to d-MAO ("dry methylaluminoxane") and found that **8** activated with d-MAO gives rise to a highly active single-site catalyst. A slight decrease in the activity has been observed with an increase in the temperature but still high enough to be called "very high activity".[12] For the less sterically protected systems **9**−**11**, comparatively lower activities have been observed. The introduction of an additional directing alkoxy ligand in **6** leads to a decrease in activity compared to **8** (Table 2, entries 4 and 9) and produces polymer with a bimodal distribution. At 80 °C, the polymerization behavior of **6** was very similar to that of **8**, probably because of a fast alkoxy-ligand transfer to aluminum, leaving the active system **8**/d-MAO behind. The selective ligand transfer has also been verified and supported by an independent synthesis of the corresponding tribenzyl complex **12**. The activity shown by complexes **6** and **8**−**11** is very high compared to that already known for aminopyridinatotitanium systems[5] and could be attributed to the steric bulk of the ligands of these complexes.

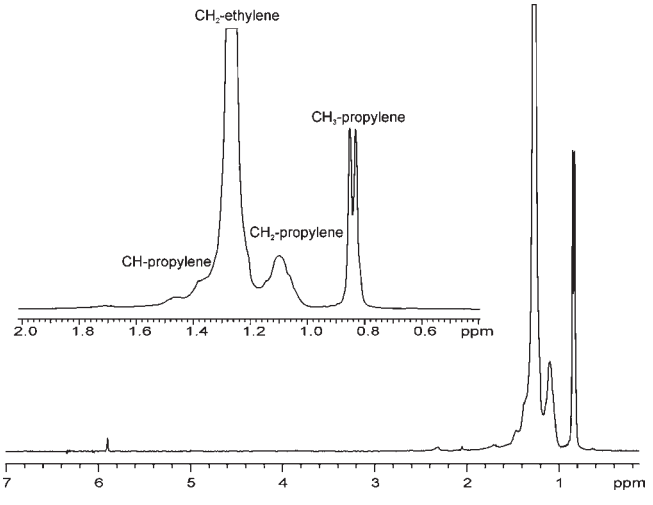

Figure 4. ^{1}H NMR spectrum of poly(ethylene-*co*-propene) obtained with the **8**/d-MAO system catalyst.

The catalyst system **8**/d-MAO shows moderate activity toward propylene polymerization (Table 3, entry 1). However, the presence of ethylene reactivates the catalyst and provides a copolymer with narrow molecular weight distribution. The ^{1}H and ^{13}C NMR spectroscopic analyses reveal

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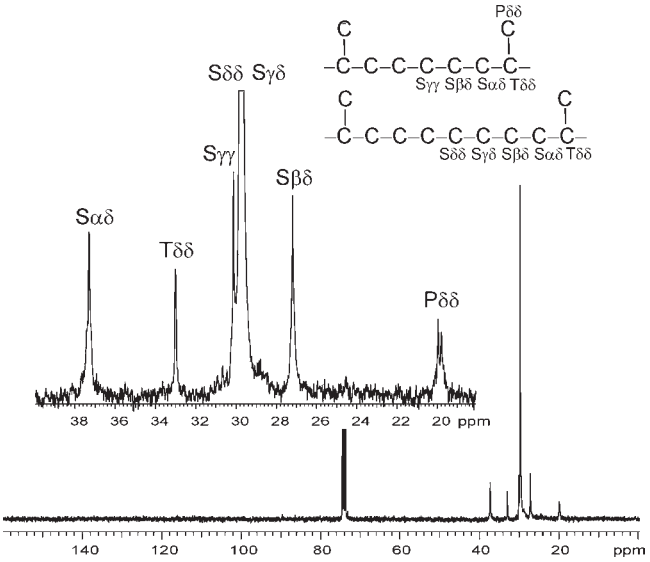

Figure 5. ^{13}C NMR spectrum of poly(ethylene-*co*-propene) (with nearly 7 mol % incorporation of propene) obtained with the **8**/d-MAO system catalyst.

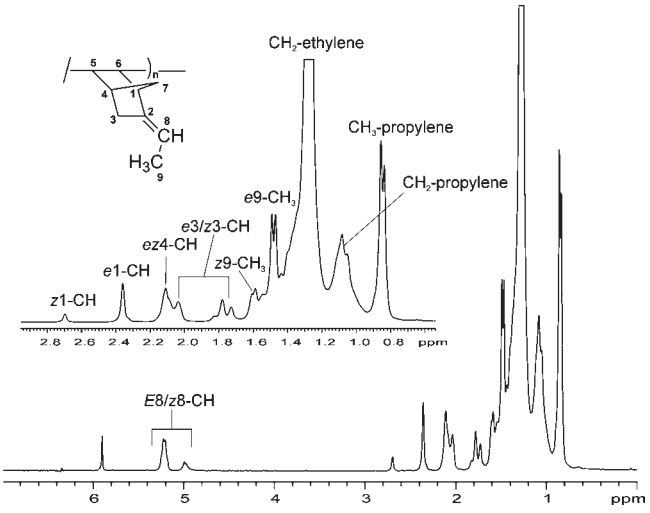

Figure 6. ^{1}H NMR spectrum of ethylene−propene−ENB terpolymer obtained with the **8**/d-MAO system catalyst.

long-chain copolymer with isolated propylene units (Figures 4 and 5).[6m]

Catalyst systems based on **9** and **10** are slightly less active compared to **8** with nearly identical molecular weights for the formed copolymers, while for the least bulky system **11**/d-MAO, a significant decrease in the activity to almost half was observed (Table 3, entry 6). It is notable that replacement of propylene by 10 mL of 1-hexene leads not to the formation of an ethylene−hexene copolymer but surprisingly to a strong enhancement of the ethylene polymerization activity (Table 3, entry 7).

After these motivating copolymerization results, we also became interested in the incorporation of cyclic olefin monomers like dicyclopentene,[13] norbornene,[14] and 5-ethylidene-2-norbornene.[15] The latter one is often used in the synthesis of highly valuable EPDM rubber polymers.[16] The addition of 10 mL of 2-ethylidenenorbornene (ENB) to the ethylene polymerization

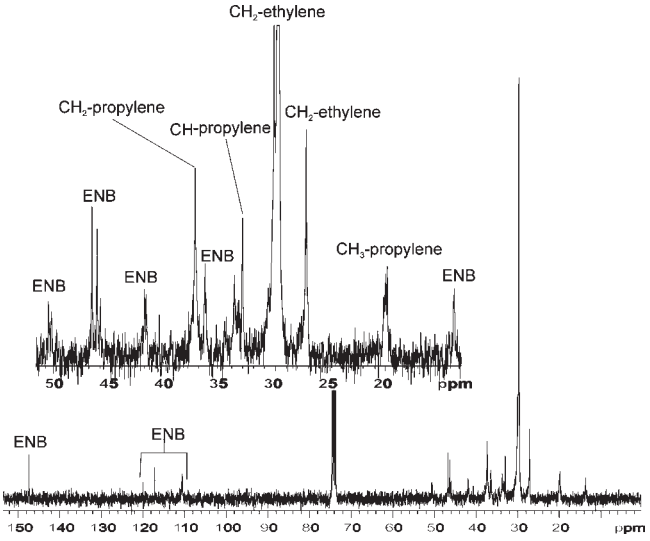

Figure 7. ^{13}C NMR spectrum of ethylene−propene−ENB terpolymer obtained with the **8**/d-MAO system catalyst.

with **8**/d-MAO (Table 3, entry 9) gives a highly active ethylene consumption, leading to a glassy transparent polymer. Unfortunately, further analysis of the polymer could not be achieved because of very fast cross-linking under air. To overcome this problem, we reduced the amount of ENB to 1 mL and switched to terpolymerization by adding additional propylene to the autoclave, yielding a rubberlike polymer that was soluble in tetrachloroethane and has been characterized by NMR spectroscopy (Figures 6 and 7).[14d,15c,15d] Besides the characteristic peaks of the ethylene/propylene (EP) copolymer, additional peaks for the incorporated ENB could be observed in the ^{13}C NMR spectra. We also observe peaks for the unreacted double bond in the olefinic region. A decrease in the activity compared to the EP copolymerization under the same conditions has been observed, but this decrease is comparatively low.

The mono(aminopyridinato)titanium catalyst systems are stable for the entire period of co- and homopolymerization (15 min) with a slight drop over time.

■ CONCLUSIONS

A series of conclusions can be drawn from the present studies. The best way to prepare mono(aminopyridinato)-titanium complexes in high yields is via amine elimination because salt elimination may lead to ring opening of coordinated THF ligands. Mono(aminopyridinato)titanium complexes show less stability in the ethylene homo- and copolymerization if activated with MAO but are highly active if MAO is replaced by d-MAO. If one applies these catalyst systems to EP copolymerization, a high regioselectivity is observed. Propylene is inserted only after ethylene, and no propylene/propylene sequences were detected. Cyclic comonomers like ENB could be incorporated to yield highly valuable EPD terpolymers.

■ EXPERIMENTAL SECTION

Synthesis and Structure Analysis. All manipulations were performed with rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual-manifold Schlenk line or in an argon-filled glovebox (mBraun 120-G) with a high-capacity recirculator (<0.1 ppm O_2).

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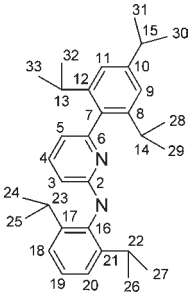
Nonhalogenated solvents were dried by distillation from sodium wire/benzophenone. $[(CH_3)_2NTiCl_3]$ was prepared according to literature procedures.[17] Commercial $[C_6H_5CH_2MgCl]$ (1.0 M in diethyl ether; Aldrich) and $[TiCl_4(THF)_2]$ and $[TiCl_4]$ (Acros) were used as received. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried, and distilled prior to use. Toluene for polymerization (Aldrich, anhydrous, 99.8%) was passed over columns of Al_2O_3 (Fluka), a BASF R3-11-supported copper−oxygen scavenger, and molecular sieves (Aldrich, 4 Å). Ethylene (AGA polymer grade) was passed over a BASF R3-11-supported copper−oxygen scavenger and molecular sieves (Aldrich, 4 Å). Poly(methylaluminoxane) (PMAO, $[MeAlO]_n$, 4.9 wt % in aluminum; Akzo) were used as received. d-MAO was prepared by the removal of all volatiles from PMAO (4.9 wt % in aluminum; Akzo). NMR spectra were recorded on a Bruker ARX 250 MHz, and chemical shifts are reported in ppm relative to the deuterated solvent. Elemental analyses (CHN) were determined using a Vario EL III instrument. X-ray crystal structure analyses were performed by using a STOE-IPDS II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement were accomplished using *SIR97*,[18] *SHELXL97*,[19] and *WinGX*.[20] Crystallographic details are summarized in Table 1

General Description of Ethylene Polymerization Experiments with MAO. The catalytic ethylene polymerization reactions were performed in a stainless steel 1 L autoclave (Medimex) in semibatch mode (ethylene was added by a replenishing flow to keep the pressure constant). The reactor was temperature- and pressure-controlled and equipped with separate toluene, catalyst, and cocatalyst injection systems and a sample outlet for continuous reaction monitoring. For up to 15 bar of ethylene pressure, multiple injections of the catalyst with a pneumatically operated catalyst injection system were used. During polymerization runs, the pressure, ethylene flow, inner and outer reactor temperatures, and stirrer speed were monitored continuously. In a typical semibatch experiment, the autoclave was evacuated and heated for 1 h at 125 °C prior to use. The reactor was then brought to the desired temperature, stirred at 600 rpm, and charged with 230 mL of toluene, together with PMAO (550 mg of a toluene solution, 4.9 wt % aluminum, 1 mmol), as was not mentioned different in the text. After pressurization with ethylene to reach 5 bar of total pressure, the autoclave was equilibrated for 5 min. Subsequently, 1 mL of a 0.002 M catalyst stock solution in toluene was injected, together with 30 mL of toluene, to start the reaction. During the run, the ethylene pressure was kept constant to within 0.2 bar of the initial pressure by a replenishing flow. After 15 min of reaction time, the reactor was vented and the residual aluminum alkyls were destroyed by the addition of 100 mL of ethanol. A polymeric product was collected, stirred for 30 min in acidified ethanol, and rinsed with ethanol and acetone on a glass frit. The polymer was initially dried in air and subsequently in vacuo at 80 °C.

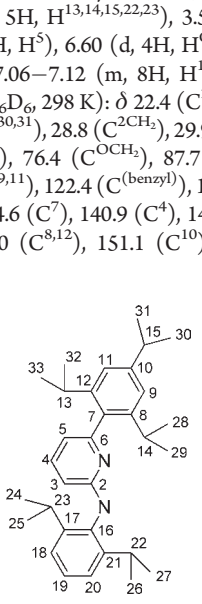
Description of EP Copolymerization Experiments. The general procedure and conditions as described above were followed, using successively 2 bar of propylene and 5 bar of ethylene to pressurize the reactor.

The polymer samples for NMR spectroscopic measurements were prepared by dissolving 15 mg of the polymer in 0.5 mL of $C_2D_2Cl_4$ at 100 °C for 3 h before measurement. Gel permeation chromatography analysis was carried out on an Agilent PL-GPC220 chromatograph, equipped with a capillary differential-pressure detector, a refractive-index detector, and a two-angle (15° and 90°) light-scattering photometer at 150 °C using 1,2,4-trichlorobenzene as the mobile phase. The samples were prepared by dissolving the polymer (0.1% w/v) in the mobile-phase solvent in an external oven and were run without filtration. The molecular weight was referenced to polyethylene (M_w = 50 000 g mol^{-1}) and polystyrene (M_w = 520−3 000 000 g mol^{-1}) standards. The reported values are the average of at least two independent determinations.

Synthesis of 6. To **1** (0.497 g, 1 mmol) and $[TiCl_4(THF)_2]$ (0.334 g, 1 mmol) was added THF (20 mL) at room temperature. The resulting maroon solution was stirred overnight. THF was evaporated to dryness, and the product was extracted with 10 mL of hexane, which upon standing at room temperature afforded dark-red crystals of the product. Yield: 0.508 g, 68%. Elem anal. Calcd for $C_{40}H_{58}Cl_3N_2O_2Ti$ (751.30): C, 63.79; H, 7.76; N, 3.72. Found: C, 63.11; H, 7.89; N, 3.78. ^{1}H NMR (C_6D_6, 298 K): δ 1.05 (d, 6H, $H^{28,29,32,33}$), 1.11 (d, 6H, $H^{30,31}$), 1.52 (d, 6H, $H^{24,25,26,27}$), 1.33 (m, 8H, H^{2CH_2}, β-CH_2, THF), 1.41 (d, 6H, $H^{24,25,26,27}$), 1.56 (d, 6H, $H^{28,29,32,33}$), 2.96 (t, 2H, H^{CH_2Cl}), 2.96 (sept, 1H, H^{15}), 3.21 (sept, 2H, $H^{13,14}$), 3.60 (br m, 6H, $H^{22,23}$, α-CH_2, THF), 4.05 (t, 2H, H^{OCH_2}), 5.50 (d, 1H, H^3), 6.63 (d, 1H, H^5), 6.93 (t, 1H, H^4), 7.17 (s, 3H, $H^{18,19,20}$), 7.22 (s, 2H, $H^{9,11}$). ^{13}C NMR (C_6D_6, 298 K): δ 23.2 ($C^{28,29,32,33}$), 24.3 ($C^{24,25,26,27}$), 24.7 ($C^{24,25,26,27}$), 25.6 ($C^{28,29,32,33}$), 26.6 (β-CH_2, THF), 28.4 ($C^{30,31}$), 28.9 ($C_{22,23}$), 29.3 (C^{2CH_2}), 31.1 ($C^{13,14}$), 34.8 (C^{15}), 44.3 (C^{CH_2Cl}), 70.0 (α-CH_2, THF), 82.8 (C^{OCH_2}), 100.3 (C^3), 119.8 (C^5), 120.8 (C^{19}), 124.4 ($C^{9,11}$), 128.2 ($C^{18,20}$) 134.0 (C^7), 140.0 (C^4), 143.6 (C^{10}), 143.7 ($C^{17,21}$), 147.6 ($C^{8,12}$), 150.0 (C^{16}), 156.0 (C^6), 164.0 (C^2).



Synthesis of 7. $[C_6H_5CH_2MgCl]$ (2.1 mL, 2.1 mmol) was added to **6** (0.475 g, 0.7 mmol) in ether (20 mL), at −30 °C as the color started changing to red. The solution mixture was allowed to reach room temperature and was further stirred for 2 h. The solution was evaporated to dryness, and the product was extracted with pentane (10 mL). Filtrate was cooled at −25 °C to afford red crystals of the product. Yield: 0.259 g, 47%. Elem anal. Calcd for $C_{50}H_{65}ClN_2OTi$ (793.38): C, 75.69; H, 8.26; N, 3.53. Found: C, 74.89; H, 8.60; N, 3.59. ^{1}H NMR (C_6D_6, 298 K): δ 1.01 (p, 4H, H^{2CH_2}), 1.10−1.36 (m, 30H, $H^{24,25,26,27,28,29,30,31,32,33}$), 2.71 and 2.82 (two doublets AB system, 4H, $H^{CH_2(benzyl)}$), 2.88 (t, 2H, H^{CH_2Cl}), 3.15 (sept, 5H, $H^{13,14,15,22,23}$), 3.59 (t, 2H, H^{OCH_2}), 5.53 (d, 1H, H^3), 6.50 (d, 1H, H^5), 6.60 (d, 4H, $H^{CH(benzyl)}$), 6.86 (t, 1H, H^4), 6.94 (t, 1H, H^{19}), 7.06−7.12 (m, 8H, $H^{18,20,CH(benzyl)}$), 7.30 (s, 2H, $H^{9,11}$). $_{13}$C NMR (C_6D_6, 298 K): δ 22.4 ($C^{28,29,32,33}$), 24.4 ($C^{24,25,26,27}$), 27.2 (C^{CH_2}), 28.7 ($C^{30,31}$), 28.8 (C^{2CH_2}), 29.9 ($C^{22,23}$), 31.6 ($C^{13,14}$), 34.9 (C^{15}), 44.9 (C^{CH_2Cl}), 76.4 (C^{OCH_2}), 87.7 ($C^{CH_2(benzyl)}$), 102.1 (C^3), 116.3 (C^5), 121.3 ($C^{9,11}$), 122.4 ($C^{(benzyl)}$), 124.0 (s, $C^{18,20}$), 126.7 (C^{19}), 127.0 ($C^{(benzyl)}$), 134.6 (C^7), 140.9 (C^4), 143.1 (C^{10}), 143.7 ($C^{(benzyl)}$), 147.2 ($C^{17,21}$), 148.0 ($C^{8,12}$), 151.1 (C^{10}), 150.5 (C^{16}), 156.5 (C^6), 167.9 (C^2).



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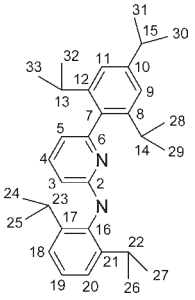
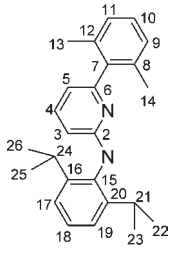
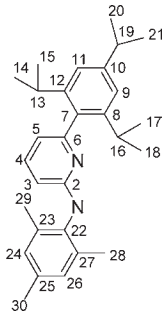
Synthesis of 8. Ether (30 mL) was added to **1** (0.913 g, 2 mmol) and $[(CH_3)_2NTiCl_3]$ (0.397 g, 2 mmol) at room temperature. The resulting purple reaction mixture was stirred overnight. The solvent was evaporated completely to give the desired purple product. Yield: 1.278 g, 98%. Elem anal. Calcd for $C_{34}H_{50}Cl_3N_3Ti$ (655.01): C, 62.34; H, 7.69; N, 6.42. Found: C, 61.78; H, 8.04; N, 6.05. ^{1}H NMR (C_6D_6, 298 K): δ 1.01 (d, 6H, $H^{30,31}$), 1.16 (m, 12H, $H^{28,29,32,33}$), 1.48 (d, 6H, $H^{24,25,26,27}$), 1.65 (d, 6H, $H^{24,25,26,27}$), 1.80 (6H, $H^{(CH_3)_2NH}$), 2.75 (sept, 1H, H^{15}), 3.02 (sept, 2H, $H^{13,14}$), 3.99 (sept, 2H, $H^{22,23}$), 5.64 (d, 1H, H^3), 6.64 (d, 1H, H^5), 6.91 (t, 1H, H^4), 7.11 (s, 2H, $H^{9,11}$), 7.23 (s, 3H, $H^{18,19,20}$). ^{13}C NMR (C_6D_6, 298 K): δ 22.6 ($C^{28,29,32,33}$), 24.2 ($C^{24,25,26,27}$), 24.9 ($C^{24,25,26,27}$), 26.9 ($C^{28,29,32,33}$), 28.2 ($C^{30,31}$), 28.7 ($C^{22,23}$), 31.2 ($C^{13,14}$), 34.8 (C^{15}), 38.83 ($C^{(CH_3)_2NH}$), 101.8 (C^3), 101.9 (C^5), 120.6 ($C^{9,11}$), 121.0 (C^{19}), 124.4 ($C^{18,20}$), 133.1 (C^7), 139.7 (C^4), 143.8 (C^{10}), 147.9 ($C^{17,21}$), 148.2 (C^{16}), 150.6 ($C^{8,12}$), 153.1 (C^6), 162.4 (C^2).



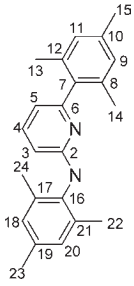
Synthesis of 9. Ether (20 mL) was added to **2** (0.358 g, 1 mmol) and $[(CH_3)_2NTiCl_3]$ (0.198 g, 1 mmol). The resulting purple solution was stirred overnight. Ether was evaporated, leaving behind a purple product, which was dried under vacuum. Yield: 0.546 g, 98%. Elem anal. Calcd for $C_{27}H_{36}Cl_3N_3Ti$ (556.82): C, 58.24; H, 6.52; N, 7.55. Found: C, 58.68; H, 6.70: N, 7.36. ^{1}H NMR (C_6D_6, 298 K): δ 1.18 (d, 6H, $H^{22,23,25,26}$), 1.64 (d, 6H, $H^{22,23,25,26}$), 1.80 (s, 6H, $H^{HN(CH_3)_2}$), 2.28 (s, 6H, $H^{13,14}$), 2.85 (br s, 1H, $H^{HN(CH_3)_2}$), 4.00 (sep, 2H, $H^{21,24}$), 5.58 (d, 1H, H^3), 6.15 (d, 1H, H^5), 6.82 (t, 1H, H^4), 6.86−7.24 (m, 6H, $H^{9,10,11,17,18,19}$). ^{13}C NMR (C_6D_6, 298 K): δ 21.0 ($C^{13,14}$), 24.7 ($C^{22,23,25,26}$), 25.0 ($C^{22,23,25,26}$), 28.7 ($C^{21,24}$), 38.8 ($C^{HN(CH_3)_2}$), 101.7 (C^3), 119.0 (C^5), 124.4 ($C^{9,11}$), 127.4 ($C^{17,19}$), 128.6 (C^{18}), 128.9 (C^{10}), 137.1 ($C^{16,20}$), 137.7 (C^4), 141.0 (C^7), 143.8 ($C^{8,12}$), 148.2 (C^{15}), 153.2 (C_6), 162.7 (C_2).



Synthesis of 10. Ether (20 mL) was added to **3** (0.829 g, 2 mmol) and $[(CH_3)_2NTiCl_3]$ (0.396 g, 2 mmol) at room temperature. The resulting purple solution was stirred overnight. The solvent was evaporated, leaving behind a purple product, which was then dried under vacuum. Yield: 1.176 g, 96%. Elem anal. Calcd for $C_{31}H_{44}Cl_3N_3Ti$ (612.93): C, 60.75; H, 7.24; N, 6.86. Found: C, 61.06; H, 7.46; N, 6.65. ^{1}H NMR (C_6D_6, 298 K): δ 1.05 (d, 6H, $H^{14,15,17,18}$), 1.19 (d, 6H, $H^{14,15,17,18}$), 1.50 (d, 6H, $H^{20,21}$), 1.84 (s, 6H, $H^{HN(CH_3)_2}$), 2.14 (s, 3H, H^{30}), 2.63 (s, 6H, $H^{28,29}$), 2.77 (m, 1H, H^{19}), 3.06 (sep, 2H, $H^{13,16}$), 5.60 (d, 1H, H^3), 6.62 (d, 1H, H^5), 6.80 (s, 2H, $H^{24,26}$), 6.85 (t, 1H, H^4), 7.13 (s, 1H, $H^{9,11}$). ^{13}C NMR (C_6D_6, 298 K): δ 20.0 ($C^{28,29}$), 20.9 (C^{30}), 22.7 ($C^{14,15,17,18}$), 24.3 ($C^{14,15,17,18}$), 26.9 ($C^{20,21}$), 31.2 ($C^{13,16}$), 34.8 (C^{19}), 38.8 ($C^{HN(CH_3)_2}$), 101.4 (C^3), 120.6 ($C^{9,11}$), 120.7 (C^5), 129.4 ($C^{24,26}$), 132.9 ($C^{23,27}$), 133.2 (C^{25}), 136.8 (C_7), 140.0 (C_4), 146.7 (C^{22}), 147.9 ($C^{8,12}$), 148.9 (C^{10}), 150.5 (C^6), 153.3 (C^2).



Synthesis of 11. **4** (0.661 g, 2 mmol) in ether (20 mL) was added to brown $[(CH_3)_2NTiCl_3]$ (0.397 g, 2 mmol) in ether (5 mL) at room temperature. A color change from brown to maroon red and then to purple was observed. The reaction mixture was stirred overnight. The solution was evaporated, leaving behind a purple product. Yield: ≈100%. Elem anal. Calcd for $C_{25}H_{32}Cl_3N_3Ti$ (528.77): C, 56.79; H, 6.10; N, 7.95. Found: C, 56.67; H, 5.97; N, 7.94. ^{1}H NMR (C_6D_6, 298 K): δ 1.85 (s, 6H, $H^{HN(CH_3)_2}$), 2.12 (s, 3H, H^{15}), 2.17 (s, 6H, H^{23}), 2.30 (s, 6H, $H^{22,24}$), 2.64 (s, 6H, $H^{13,14}$), 5.59 (dd, 1H, H_3), 6.24 (dd, 1H, H^5), 6.72 (s, 2H, $H^{18,20}$), 6.80−6.87 (m, 4H, $H^{4,9,11,NH}$). ^{13}C NMR (C_6D_6, 298 K): δ 19.9 ($C^{22,24}$), 20.8 ($C^{13,14}$), 20.9 (C^{23}), 21.0 (C^{15}), 38.8 ($C^{N(CH_3)_2}$), 101.1 (C^3), 119.1 (C^5), 128.1 ($C^{9,11}$), 129.4 ($C^{18,20}$), 132.9 (C^7), 135.2 (C^4), 136.8 (C^{16}), 138.4 ($C^{17,21}$), 141.1 ($C^{8,12}$), 148.9 (C^{10}), 153.7 (C^6), 161.0 (C^2).



Synthesis of 12. To **8** (0.6 g, 0.92 mmol) in ether (20 mL) was added $[C_6H_5CH_2MgCl]$ (2.78 mL, 2.78 mmol) at −30 °C as the color started to change to red. The solution mixture was allowed to reach room temperature and was further stirred for 2 h. The solution was evaporated to dryness, and the product was extracted with hexane (10 mL). The filtrate was cooled at −25 °C to afford a red crystalline material of the product. Yield: 0.43 g, 55%. Elem anal. Calcd for $C_{53}H_{64}N_2Ti$ (776.96): C, 81.93; H, 8.30; N, 3.61. Found: C, 80.61; H, 8.37; N, 3.44. ^{1}H NMR (C_6D_6, 298 K): δ 1.06 (d, 6H, $H^{28,29,32,33}$), 1.13 (d, 6H, $H^{30,31}$), 1.22 (m, 12H, $H^{24,25,26,27}$), 1.27 (d, 6H, $H^{28,29,32,33}$), 2.80 (sept, 3H, $H^{13,14,15}$), 3.10 (s, 6H, H^{CH_2}), 3.68 (sept, 2H, $H^{22,23}$), 5.74 (dd, 1H, H^3), 6.23 (dd, 1H, H^5), 6.51 (d, 6H, $H^{CH(benzyl)}$), 6.81 (t, 1H, H^4), 6.87−7.18 (m, 12H, $H^{18,19,20,CH(benzyl)}$), 7.26 (s, 2H, $H^{9,11}$). ^{13}C NMR (C_6D_6, 298 K): δ 22.4 ($C^{28,29,32,33}$), 23.9 ($C^{24,25,26,27}$), 24.3 ($C^{30,31}$), 25.5 ($C^{24,25,26,27}$), 26.6 ($C^{28,29,32,33}$), 29.1 ($C^{22,23}$), 31.1 ($C^{13,14}$), 34.9 (C^{15}), 104.4 (C^3), 107.9 ($C^{CH_2(benzyl)}$), 116.0 (C^5), 121.4 ($C^{9,11}$), 123.6 ($C^{(benzyl)}$), 124.8 ($C^{18,20}$), 127.2 (C^{19}), 128.9 ($C^{(benzyl)}$), 134.4

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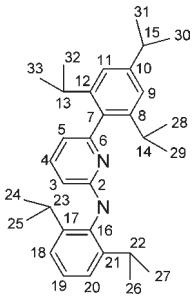
(s, C^{7}), 140.7 (C^{4}), 144.8 ($C^{17,21}$), 145.6 (C^{16}), 148.0 ($C^{(benzyl)}$), 146.8 ($C^{8,12}$), 150.5 (C^{10}), 156.0 (C^{6}), 170.2 (C^{2}).



■ ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic data for compounds **6** (CCDC 813068), **7** (CCDC 813069), **8** (CCDC 813070), and **11** (CCDC 813067). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ NOTE ADDED AFTER ASAP PUBLICATION

Due to a production error, this paper was published on the Web on April 12, 2011, with Figure 7 duplicated. The corrected version was reposted on April 14, 2011.