Polymerization

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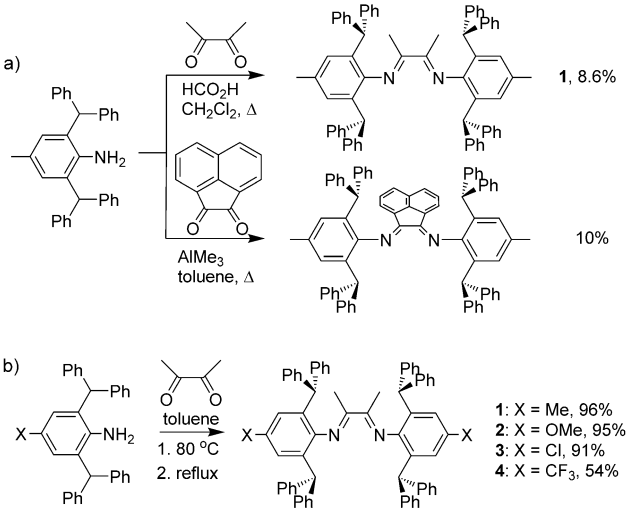
Highly Robust Palladium(II) α-Diimine Catalysts for Slow-Chain-Walking Polymerization of Ethylene and Copolymerization with Methyl Acrylate**

*Shengyu Dai, Xuelin Sui, and Changle Chen**

Abstract: *A series of sterically demanding α-diimine ligands bearing electron-donating and electron-withdrawing substituents were synthesized by an improved synthetic procedure in high yield. Subsequently, the corresponding Pd complexes were prepared and isolated by column chromatography. These Pd complexes demonstrated unique properties in ethylene polymerization, including high thermal stability and high activity, thus generating polyethylene with a high molecular weight and very low branching density. Similar properties were observed for ethylene/methyl acrylate copolymerization. Because of the high molecular weight and low branching density, the generated polyethylene and ethylene/methyl acrylate copolymer were semicrystalline solids. The (co)polymers had unique microstructures originating from the unique slow-chain-walking activity of these Pd complexes.*

In the 1990s, Brookhart and co-workers reported the seminal discovery that bulky α-diimine–nickel/palladium complexes could generate high-molecular-weight polyethylene and incorporate polar functionalized monomers into polyolefins.[1] Since then, there has been tremendous interest in exploring new late-transition-metal catalysts for olefin polymerization and copolymerization with polar monomers.[2,3] Despite their unique properties, these catalysts suffer from poor thermal stability, which has greatly limited their potential industrial application (70–110 °C).[4] At temperatures above 50 °C, they undergo fast decomposition, and the molecular weight of the synthesized polymers is greatly reduced.[5] This behavior is mainly attributed to increased associative chain transfer, C–H activation of the ligand, potential decomposition of the metal hydride species generated in situ, and bisligation.[6] Other major limitations of these catalysts include a large decrease in catalytic activity and polymer molecular weight in the presence of polar monomers. Furthermore, the amorphous nature of the (co)polymers as a result of their high branching density limits their potential application to very specific areas.

There have been numerous studies to address these issues. In the field of nickel(II) α-diimine complexes, significant advances have been made through modification of the ligand backbone and the *N*-aryl substituents.[7] For example, Ionkin and Marshall reported the synthesis of *ortho*-difurylaryl-substituted nickel α-diimine catalysts, which exhibited ethylene-polymerization activity even at 150 °C.[8] The Ni^{II} complexes containing camphorquinone-derived ligands reported by Wu and co-workers showed moderate stability up to 80 °C.[9] Recently, the use of benzhydryl-derived ligand frameworks enabled the generation of highly stable Ni catalysts.[10] In particular, Long and co-workers reported the synthesis of a sterically demanding nickel(II) α-diimine complex by the use of 2,6-bis(diphenylmethyl)-4-methylaniline (Scheme 1a); the resulting catalyst was capable of producing well-defined polyethylene at temperatures up to 100 °C.[11] The exceptional thermal stability of this catalyst makes it appropriate for industrially used gas-phase polymerization (80–100 °C). However, the low synthetic yield for the 2,3-butadione-derived ligand (Scheme 1a, 8.6 %) is an obviously bottleneck for its wide application. The same research group recently reported a modified synthetic procedure for an acenaphthenequinone-derived ligand, which was still only obtained in 10 % yield (Scheme 1b).[12]



Scheme 1. a) Reported procedure for the synthesis of α-diimine ligand **1**. b) Improved synthesis of ligands of this type with different substituents.

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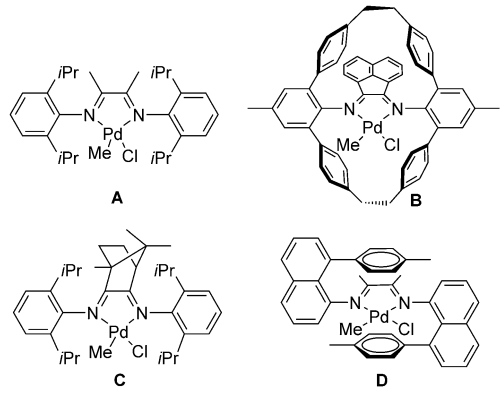


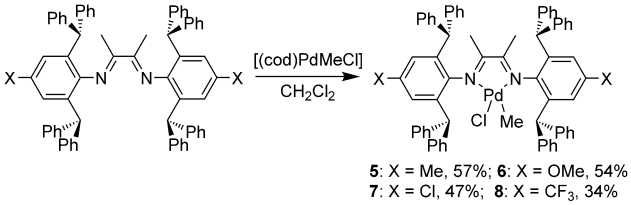
Scheme 2. Previously reported palladium α-diimine catalysts.

In contrast, there has been much less success in enhancing the thermal stability of palladium(II) α-diimine complexes (Scheme 2, **A**). Guan and co-workers showed that the presence of electron-donating substituents can increase the thermal stability of palladium(II) α-diimine complexes.[13] The same research group reported that cyclophane-based palladium(II) α-diimine complexes (Scheme 2, **B**) remained active in ethylene polymerization at 60 °C.[14] These palladium complexes incorporated a much higher amount of methyl acrylate (MA) comonomers than the acyclic analogue. The difference in activity is proposed to originate from the inhibition of olefin exchange as a result of a steric effect.[15] Wu and co-workers reported that Pd^{II} complexes with camphorquinone-derived ligands (Scheme 2, **C**) displayed moderate activity at up to 70 °C.[6c] Recently, Brookhart and co-workers studied the olefin-polymerization properties of a "sandwich"-type diimine palladium catalyst (Scheme 2, **D**).[16] Interestingly, these complexes share some common properties and limitations. First of all, they are all much less active (even by an order of magnitude) than complex **A** at low temperatures. Second, they generate polyethylene or ethylene/methyl acrylate (E–MA) copolymer with a much lower molecular weight than those synthesized with complex **A**. Third, they have similar or greater chain-walking capabilities as compared with complex **A**, thus affording polymers with similar or higher branching density. Therefore, the polymer or copolymer generated is completely amorphous and is usually a liquid or wax at room temperature.

Herein, we report a modified procedure to synthesize ligand **1** in much higher yield (Scheme 1b). With this improved synthesis and its excellent properties, the Ni^{II} complex based on **1** may stimulate more research interest in the search for industrially appropriate, robust late-transition-metal olefin-polymerization catalysts. We also report the synthesis of the series of ligands **1**–**4** bearing electron-donating and electron-withdrawing substituents by this improved synthetic procedure. Finally, Pd^{II} complexes of ligands **1**–**4** showed exceptional thermal stability and activity in ethylene polymerization and E–MA copolymerization. To the best of our knowledge, the Pd^{II} complex bearing ligand **2** is the most thermally stable and most active palladium(II) α-diimine catalyst ever reported.

The low yield of the reaction shown in Scheme 1a for the synthesis of **1** was proposed to originate from the low reaction temperature in CH_2Cl_2. However, when we attempted the synthesis in toluene in the presence of HCO_2H or *p*-toluenesulfonic acid, no product at all was formed, probably because 2,3-butadione escapes when the reaction mixture is heated at reflux. Therefore, a two-step procedure was designed (Scheme 1b). The reaction mixture was first heated at 80 °C for 24 h, after which time 1 equivalent of the aniline substrate and 1 equivalent of the monocondensation product were present. The escape of 2,3-butadione was efficiently avoided in this way. Subsequently, the mixture was heated at reflux in toluene to yield analytically pure **1** in 96% yield. Ligands **2** and **3** were prepared by the same procedure in 95 and 91% yield. In the synthesis of ligand **4**, the aniline starting material had been consumed by the end of the reaction. The low yield (54%) is probably due to the decomposition of the reaction intermediate or the α-diimine product. These ligands can be readily obtained on a 10 g or bigger scale on the basis of this improved synthetic procedure.

The synthesis of the Pd^{II} complexes is not trivial at all (Scheme 3a). Monitoring of the reaction of ligand **1** (1 equiv)



Scheme 3. Synthesis of the Pd^{II} complexes **5**–**8**. cod = 1,5-cyclooctadiene.

with [(cod)PdMeCl] (1 equiv) by ^1H NMR spectroscopy indicated the generation of two major Pd^{II} species in a roughly 1:1 ratio. One product was complex **5**, and the other product was not identified, but may correspond to the complexation of the ligand to Pd^{II} through one imine nitrogen atom. Complex **5** could be isolated in 9% yield by multiple recrystallization or in 57% yield by column chromatography. Complexes **6**–**8** were synthesized and isolated by a similar procedure in 34–54% yield. Complexes **5**–**8** were characterized by ^1H and ^{13}C NMR spectroscopy, ^1H–^{13}C HSQC spectroscopy, and elemental analysis. Previously, the research groups of Jordan and Guan successfully obtained the methyl palladium(II) species by the treatment of ligands with $[(MeCN)_2PdCl_2]$, followed by methylation with $SnMe_4$.[15a,17] However, the reaction of ligand **2** with $[(MeCN)_2PdCl_2]$ (1 equiv) afforded multiple products in our case (see Figure S1 in the Supporting Information).

The reaction of complexes **5**–**8** with sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (NaBAF; 1 equiv) in the presence of CO led to the formation of palladium carbonyl complexes (see Scheme S1 in the Supporting Information), which were characterized by NMR and IR spectroscopic analysis. The CO stretching frequencies were redshifted with electron-donating ligands, in good correlation with the

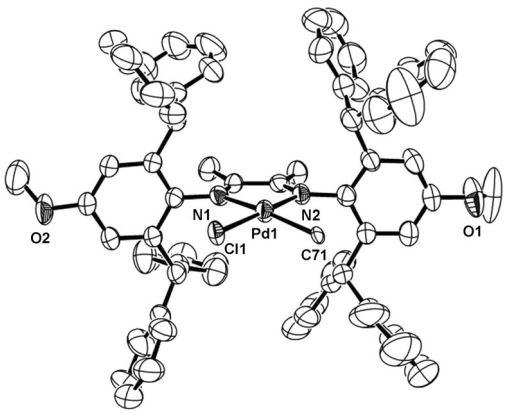


Figure 1. Molecular structure of **6**. Hydrogen atoms have been omitted for clarity. Atoms are drawn at the 30% probability level.

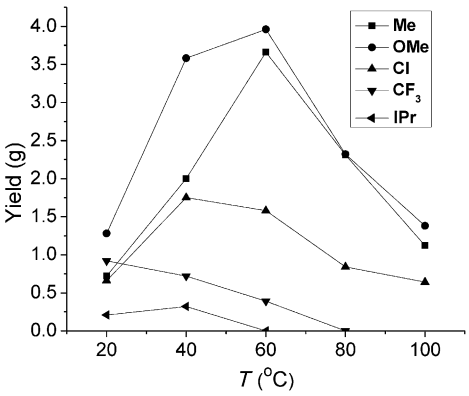


Figure 2. Polymer yield versus temperature for catalysts **5**–**8** and **A** at 20, 40, 60, 80, and 100 °C (Table 1).

Hammett substituent constant (see Figure S2). This result is expected, since an electron-rich metal center leads to stronger metal-to-CO π donation. Also, it clearly demonstrates the strong ligand electronic effect on the Pd complexes.

In the X-ray crystal structure of complex **6** (Figure 1), the observed bond lengths [Å] are typical for palladium(II) α-diimine complexes: Pd1–C71 2.114(6), Pd1–Cl1 2.268(3), Pd1–N1 2.067(6), Pd1–N2 2.070(7). The Pd center adopts a square-planar geometry with a N1-Pd1-N2 angle of 78.8(2)°, a N2-Pd1-C71 angle of 96.0(4)°, a C71-Pd1-Cl1 angle of 88.9(3)°, and a N1-Pd1-Cl1 angle of 95.8(2)°. The effective blockage of the axial positions at the Pd center is apparent from the structure.

In the study of ethylene polymerization and ethylene/MA copolymerization, a direct in situ activation procedure was employed. The (co)polymerization was initiated by the addition of NaBAF (1.2 equiv) to complexes **5**–**8** in the presence of ethylene or an E–MA mixture. The classic Pd complex **A** was prepared and studied for comparison. All of the complexes were much more active (up to an order of magnitude) than **A** under the same conditions (Table 1). Specifically, the electron-rich complexes **5** and **6** showed high thermal stability. They reached their highest activity at 60 °C and maintained high activity even at 100 °C (Figure 2). In contrast, complex **A** is not active at all above 60 °C. Also, complexes **5** and **6** were stable for more than 20 min at 80 °C during ethylene polymerization (see Table S1 and Figure S3 in the Supporting Information). Because of the higher activity and thermal stability of **5** and **6**, the polyethylene obtained by the use of these complexes (semi-crystalline solid) was much whiter than that obtained with complex **A** (sticky oil; see Figure S4).

Besides the much higher stability and activity of complexes **5**–**8**, the molecular weight of polyethylene generated with these complexes was much higher than that of polyethylene generated with complex **A**. Enhancement in molecular weight by factors of approximately 3–12 was observed (Table 1; see also Figure S5). Most interestingly, the branching density of the polyethylene generated by complexes **5**–**8** (23–29/1000 C) was much lower than that observed with complex **A** (>100/1000 C). Almost all previously reported palladium α-diimine complexes generated polyethylene with

Table 1: Effect of temperature on ethylene polymerization.[a]

Entry	Cat.	*T* [°C]	Yield [g]	Activity [10^5 g (mol Pd)$^{-1}$ h^{-1}]	M_n[b] ($\times 10^{-4}$)	PDI	T_m[c] [°C]	% C[d]	*B*[e]
1	**5**	20	0.72	5.8	14.0	1.16	99	26	25
2	**5**	40	2.00	16.0	34.5	1.26	96	21	27
3	**5**	60	3.66	29.3	9.4	1.62	91	20	28
4	**5**	80	2.31	18.5	7.2	2.10	93	20	27
5	**5**	100	1.12	9.0	3.8	1.96	92	20	27
6	**6**	20	1.28	10.2	25.3	1.11	98	34	23
7	**6**	40	3.58	28.6	53.8	1.14	98	24	25
8	**6**	60	3.96	31.7	8.2	1.77	94	21	26
9	**6**	80	2.32	18.6	6.9	1.88	92	20	27
10	**6**	100	1.38	11.0	4.6	1.98	90	19	27
11	**7**	20	0.66	5.3	12.2	1.13	97	19	29
12	**7**	40	1.75	14.0	27.7	1.42	93	18	29
13	**7**	60	1.58	12.6	16.8	1.62	89	18	27
14	**7**	80	0.84	6.7	11.2	1.64	89	18	27
15	**7**	100	0.64	5.1	6.4	1.68	86	16	29
16	**8**	20	0.92	7.4	24.4	1.42	89	19	28
17	**8**	40	0.72	5.8	10.0	1.83	91	19	28
18	**8**	60	0.39	3.1	12.0	2.68	87	17	28
19	**8**	80	trace	–	–	–	–	–	–
20	**A**	20	0.21	1.7	4.6	1.88	–[f]	–[f]	95
21	**A**	40	0.32	2.6	5.1	1.64	–[f]	–[f]	95
22	**A**	60	trace	–	–	–	–	–	–

[a] Reaction conditions: precatalyst (5 μmol), NaBAF (1.2 equiv), CH_2Cl_2 (2 mL), toluene (48 mL), 9 atm, 15 min. [b] Molecular weight was determined by GPC in trichlorobenzene at 150 °C with polystyrene standards. [c] Melting temperature was determined by differential scanning calorimetry (DSC; second heating). [d] Percent crystallinity as determined by DSC analysis. [e] Number of branches per 1000 carbon atoms, as determined by ^{1}H NMR spectroscopy.[18] [f] Completely amorphous polymer. PDI = polydispersity index.

branching numbers well above 80. Therefore, the low branching numbers in the 20s observed with complexes **5**–**8** are extremely unusual. Because of the high molecular weight and low branching density, the polyethylene generated by these complexes is semicrystalline, with a melting temperature approaching 100 °C. Polyethylene with these properties has rarely been synthesized previously with palladium α-diimine complexes.

As mentioned above, all previous modifications of complex **A** led to reduced activity, lower polymer molecular weight, and similar or higher branching density. In this sense, complexes **5**–**8** possess unique and quite surprising properties in ethylene polymerization. As compared to complex **A**, these complexes demonstrate much greater thermal stability, higher activity by up to an order of magnitude, and the generation of polymers with higher molecular weight by up to an order of magnitude and lower branching density by a factor of approximately 4. The property of greater thermal stability can be understood readily. The diphenylmethyl groups block the axial position more efficiently than the isopropyl groups in complex **A**, thus slowing down the potential catalyst-decomposition pathways.[5,6] This strategy has been successfully applied previously, for example, in cyclophane-based palladium(II) α-diimine complexes (Scheme 2, **B**) and the "sandwich" diimine palladium catalyst **D**, all of which showed enhanced thermal stability. However, both **B** and **D** showed lower activity and provided polyethylene with a lower molecular weight. For example, the reduction in activity by a factor of approximately 10 and reduction in polymerization molecular weight by a factor of about 2 found with complex **D** as compared to the classic complex **A** was attributed to the significantly slower ethylene insertion rate by complex **D**.[16] Also, the sterically highly bulky complexes **B** and **D** generated polyethylene with branching numbers (ca. 110/1000 C) higher than that observed with the classic complex **A**. Currently, the opposite trend observed with complexes **5**–**8** is not fully understood, and it clearly cannot be explained simply on the basis of a steric effect. It is possible that the unique structures of these complexes facilitate the ethylene-trapping and -enchainment step, which therefore outcompete the chain-transfer and chain-walking steps. As the catalyst spends more time enchaining ethylene than chain walking along the polymer chain, polymers with higher molecular weight, higher activity, and lower branching density are obtained.

In the ethylene/MA copolymerization study (Table 2), similar trends were observed to those for ethylene homopolymerization. As compared to complex **A** under the same conditions, the activity of complexes **5** and **6** was up to an order of magnitude higher, the copolymer molecular weight was up to 6 times higher (see Figures S6 and S7 for a comparison of the copolymer yield and molecular weight with these catalysts), and the copolymer branching density was about 3 times lower. Also, much greater thermal stability was observed. Complexes **5** and **6** showed appreciable activity at 60 °C, whereas complex **A** completely decomposes under these conditions.[19] The MA-incorporation ratio is lower for complexes **5** and **6** than for complex **A**. However, the differences became smaller at higher temperatures. The low MA-incorporation ratio probably originates from the steric bulk of the ligands, which makes monomer binding more unfavorable for MA. Because of the high molecular weight and low branching density of these copolymers, a melting temperature of 50–70 °C was observed. Again, such a high melting temperature has not been observed previously for E–MA copolymers synthesized with a palladium α-diimine catalyst (the difference between the copolymers obtained with complexes **5** and **6** (semicrystalline solid) and complex **A** (sticky oil) can be clearly seen in Figure S8). Complexes **7** and **8** are not suitable for the copolymerization. Presumably, the electron-withdrawing groups make the Pd center more electrophilic and therefore more prone to catalyst poisoning by the polar groups.

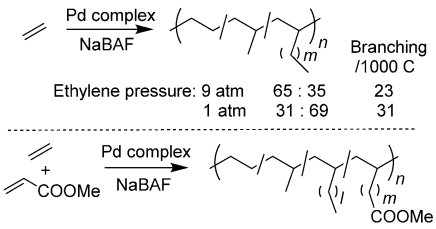
With the classic α-diimine palladium complex **A** and complex **D**, hyperbranched (branch on branch) and even dendritic polymers are produced, with randomly distributed branches, including Me, Et, *i*Pr, *n*Bu, *s*Bu, and long-chain branches. Furthermore, the catalytic activity, molecular weight of the polymer, branching density, and distribution of short-chain branches are relatively independent of ethylene pressure.[2a,3a,b,16] As a result, it is very difficult to control the polymerization process and the properties of the resulting (co)polymer by the use of different polymerization conditions. In contrast, the catalytic activity and polymer molecular

Table 2: Ethylene/MA copolymerization.[a]

Entry	Cat.	[MA] [M]	T [°C]	Yield [g]	Activity [10^3 g (mol Pd)$^{-1}$ h^{-1}]	X_{MA}[b] [%]	M_n[c] ($\times 10^{-3}$)	PDI	B[d]	T_m[e] [°C]
1	**5**	–	20	19.3	128	–	98.0	2.13	32	73
2	**5**	1	20	0.55	3.7	0.4	18.9	1.78	34	71
3	**5**	1	40	0.32	2.1	1.1	3.8	3.45	36	61
4	**5**	1	60	0.21	1.4	1.7	3.0	1.88	50	51
5	**5**	2	40	0.32	2.1	1.8	3.0	1.81	40	52
6	**6**	–	20	17.7	118	–	89.5	2.46	31	75
7	**6**	1	20	0.65	4.3	0.5	10.8	1.53	35	72
8	**6**	1	40	0.44	2.9	1.6	3.53	2.28	42	60
9	**6**	1	60	0.19	1.3	2.9	3.87	1.81	43	52
10	**6**	2	40	0.25	1.7	3.3	3.43	1.91	46	53
11	**A**	–	20	4.21	28	–	28	3.66	105	–
12	**A**	1	20	0.05	0.33	3.2	3.1	1.51	93	–
13	**A**	1	40	0.13	0.87	3.3	2.7	1.76	93	–
14	**A**	1	60	trace	–	–	–	–	–	–
15	**A**	2	40	0.03	0.20	5.8	2.5	1.89	105	–

[a] Reaction conditions: precatalyst (0.010 mmol), NaBAF (1.2 equiv), total volume of toluene and MA: 25 mL, 1 atm, 15 h. [b] Amount of MA incorporated (mol%). [c] Molecular weight was determined by GPC in trichlorobenzene at 150 °C with polystyrene standards. [d] Number of branches per 1000 carbon atoms, as determined by ^{1}H NMR spectroscopy. Branches ending with a functional group were added to the total number of branches. [e] Melting temperature was determined by differential scanning calorimetry (DSC).

weight are more responsive towards ethylene pressure in this class of catalysts (see Table S2 and Figures S9 and S10); also, only methyl and long-chain branches were observed in our system. Surprisingly, both the branching density and the short-chain distribution could be modulated to some extent by ethylene pressure (Scheme 4; see also Figures S53 and S54 and Table S3).



Scheme 4. Molecular structure of the obtained polyethylene and E–MA copolymer.

The polymers obtained at different pressures also showed dramatically different mechanical properties. At 9 atm, the polymer showed a higher modulus and low deformation, whereas the polymer obtained at 1 atm showed elastomeric behavior with a strain at break of around 550% (Figure 3). Clearly, the mechanical properties are significantly influenced by the branching density and the distribution of short-chain and long-chain branches.

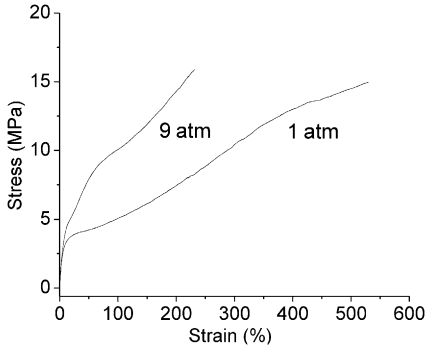


Figure 3. Stress–strain curves of the polymers obtained at different pressures (Table 1, entry 6 and Table 2, entry 6).

The microstructure of the obtained polymer can be viewed as an ethylene–propylene–α-olefin terpolymer. This type of terpolymer can be obtained by copolymerization of the three monomers with metallocene catalysts[20] or by the polymerization of an α-olefin monomer with a α-diimine nickel catalyst.[3h] The ^{13}C NMR spectrum of the polymer obtained with our system is almost the same as those observed for polymers obtained with the above-mentioned two systems (see Figure S56). As far as we know, the generation of a polymer with this microstructure by the use of only ethylene as the feedstock has not been reported previously.

The obtained E–MA copolymer had a similar microstructure to that of the polyethylene synthesized with this system, with MA units located mainly at the end of long-chain branches, and is a novel E–MA copolymer microstructure. A control experiment was carried to confirm our assignments: The ^{13}C NMR spectrum of an ethylene–undecylenic acid methyl ester copolymer agreed very well with the ^{13}C NMR spectrum of the E–MA copolymer (Figure S57). For comparison, the classic α-diimine palladium system affords amorphous hyperbranched copolymers with MA units at the end of branches; the double-decker α-diimine dipalladium complex reported by Takeuchi and co-workers generates branched copolymers containing part of the acrylate units in the polymer main chain;[21] a phosphine–sulfonate palladium system affords copolymers with MA units in the main chain.[22]

To conclude, we studied ethylene polymerization and E–MA copolymerization with benzhydryl-derived palladium α-diimine catalysts. First of all, a new synthetic strategy was developed to prepare these sterically very demanding ligands in a much more efficient fashion. Next, a series of Pd complexes bearing electron-donating and electron-withdrawing substituents were prepared, isolated, and analyzed. In comparison with the classic Pd complex **A**, these Pd complexes showed very interesting and surprising properties in ethylene polymerization, including greatly enhanced thermal stability, much higher activity (up to $3.2\times10^6\,g\,(mol\,Pd)^{-1}\,h^{-1}$), and the generation of polyethylene with a much higher molecular weight (M_n up to 538000) and much lower branching density (23–29/1000 C). Finally, these complexes showed similar properties in ethylene/MA copolymerization, including high thermal stability and activity, and the generation of copolymers with high molecular weight and low branching density. For the first time with the palladium α-diimine class of catalysts, the polyethylene and E–MA copolymer generated were semicrystalline solids. Furthermore, they had unique microstructures originating from the slow-chain-walking behavior of these catalysts.

Keywords: chain-walking polymerization · copolymerization · diimine ligands · palladium catalysis · polar monomers

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