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Amine-imine palladium catalysts for living polymerization of ethylene and copolymerization of ethylene with methyl acrylate: Incorporation of acrylate units into main chain and branch end

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Neutral and cationic palladium complexes bearing amine-imine ligand with different donor functionalities have been synthesized and characterized. Cationic amine-imine palladium complexes can be directly employed in homopolymerization of ethylene and copolymerization of ethylene and methyl acrylate (MA) without any cocatalysts. A thermally stable amine-imine palladium catalyst with two bulky 2,6-diisopropyl substituents can catalyze ethylene polymerization in a living fashion at 25 °C to afford branched polyethylene. Copolymerization of ethylene and MA using a bulky amine-imine palladium catalyst affords branched copolymers with a 3-fold increased incorporation of MA relative to those obtained by α-diimine palladium analogue. Both direct incorporation of an acrylate unit into main chain and migratory incorporation of terminal acrylate unit can be observed.

Introduction

The discovery of late transition metal nickel and palladium catalysts has initiated a new olefin polymerization field because it leads to the formation of new polymeric materials which are hardly produced with early transition metal catalysts.[1] Nickel and palladium catalysts with sterically bulky axial substituents can usually produce high-molecular-weight polyethylenes with different polymer topologies (linear, hyperbranched, and dendritic structure) and the poly(α-olefin)s with various types of branches.[2] Alternatively, nickel and palladium catalysts are also ideal candidates for direct copolymerizations of ethylene with polar monomers to afford the copolymers possessing functional groups in a single step because of their good tolerance toward polar functionality.[3]

Currently, there are numerous researches on design and synthesis of nickel catalysts by ligating various ligands for olefin oligomer/polymerization, especially [N,N] bidentate ligands.[4] Steric and electronic effects of N-aryl moieties and backbone substituent effects on reactivity of olefin polymerization have been extensively studied.[4] In comparison with nickel catalysts, few ligands can be used to ligate palladium metal to form active palladium catalysts for homo- and copolymerization of ethylene because of more electron-rich metal center. Two noteworthy examples are cationic α-diimine palladium catalyst (Brookhart-type) that can produce highly branched polyethylene (PE) [3a,5] and neutral phosphine-sulfonato palladium catalyst (Drent-type) that is capable of producing linear PE.[3i,j,6] Copolymerization of ethylene with polar vinyl monomers can usually produce a highly branched polymer containing polar groups at the end of the branches using α-diimine palladium catalyst,[3a] whereas can yield a linear copolymer with polar groups built into the polyethylene main chain using phosphine-sulfonato palladium catalyst.[7] These differences of polymer microstructure highlight the powerful ligand influence on the reactivity of palladium catalysts and the potential reward for continued efforts to uncover new type of ligands and catalysts.

A new type of amine-imine ligand has been recently developed and used to ligate nickel metal to form catalyst precursor for olefin polymerizations by our group.[8] Unlike α-diimine nickel catalyst, amine-imine nickel catalyst bears two different coordinating functionalities (imine (sp^2) and amine (sp^3)), which can afford a distinct influence to the metal in the regards of both polymer structure and reactivity control. Living polymerization of ethylene was achieved using a bulky amine-imine nickel catalyst at elevated temperature up to 65 °C to produce branched polymers,[8a,b] and ligand directed regioselectivity involving insertion fashion and chain walking in amine-imine nickel-catalyzed α-olefin polymerization was clearly observed.[8f] Encouraged by the notable features of amine-imine nickel catalyst, amine-imine palladium catalysts were herein synthesized and explored for ethylene homopolymerization and copolymerization of ethylene with methyl acrylate (MA). A bulky amine-imine palladium catalyst is thermally stable at temperature as high as 45 °C as compared with related α-diimine palladium catalyst, and can catalyze ethylene polymerization in a living fashion at 25 °C. Copolymerizations of ethylene and methyl acrylate (MA)

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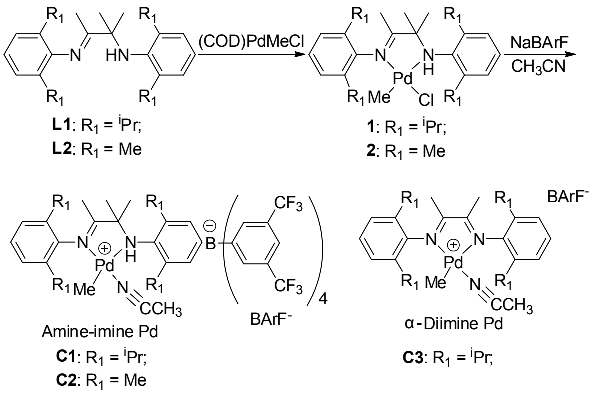
† Electronic Supplementary Information (ESI) available: [Detailed ^{1}H NMR spectra of amine-imine palladium complexes, crystal data of **1** and **C1**, CIF files for **1** and **C1**, and ^{13}C NMR spectra of polymer.]. See DOI: 10.1039/b000000x/.

with this new kind of palladium catalyst afford branched ethylene-MA copolymers with terminal and main chain acrylate units, which is different from those produced by copolymerization obtained by α-diimine palladium catalyst and phosphine-sulfonato palladium catalyst.

Results and discussion

Synthesis and characterization of amine-imine palladium complexes

Neutral chloromethylpalladium complexes (**1** and **2**) can be easily obtained by complexation of amine-imine ligands (**L1** and **L2**) and Pd(COD)MeCl (COD: 1,5-cyclooctadiene) (Scheme 1). In principle, there are two geometrical isomers (*cis*- and *trans*-isomers) for the chloromethylpalladium complexes bearing amine-imine ligands. However, ^{1}H and ^{13}C NMR spectra of the obtained chloromethylpalladium complexes confirm that only one isomer exists in the solution (see Figures S1-2 in Supporting Information (SI)). Only one proton resonance at 0.36 and 0.25 ppm in the ^{1}H NMR spectroscopy and one carbon resonance at 1.18 and 0.15 ppm in the ^{13}C NMR spectroscopy can be assigned to palladium-bound methyl groups of **1** and **2**, respectively. Single crystal X-ray diffraction analysis of **1** (Figure 1) further confirms that chloromethylpalladium complex **1** is present as a *trans* chelate isomer and features the methyl group *cis* to the imine group. Generally, palladium complex **1** displays a distorted square-planar coordination around palladium center. Pd-N2(imine) bond length is around 2.06 Å while Pd-N1(amine) bond length is around 2.23 Å, suggesting the stronger donor ability of imine.



Scheme 1 Synthesis of amine-imine palladium complexes.

These two chloromethylpalladium complexes were further treated with acetonitrile and sodium tetrakis (3,5-bis(trifluoromethyl)phenyl)borate (NaBArF) to yield cationic palladium complexes [(amine-imine)Pd(CH$_3$CN)Me]$^+$BArF$^-$ (**C1** and **C2**). Unlike chloromethylpalladium complexes, ^{1}H and ^{13}C NMR spectroscopies clearly show that cationic palladium complexes **C1** and **C2** exist two geometrical isomers (*trans*- and *cis*-isomers) in the solution (see Figures S3-4 in SI). The ratios of *trans*-isomer to *cis*-isomer can be separately calculated to 0.8/1 and 1.8/1 for **C1** and **C2** under the measured conditions. Obviously, *cis*-isomer of palladium complex appears in solution when large-dimension CH$_3$CN molecule is used as auxiliary ligand instead of chloride, which is a result of steric interactions of CH$_3$CN with *ortho* isopropyl groups on amine-bound aniline moiety. Reducing the steric hindrance of the N-aryl substituents by substituting of *o*-methyl groups for *o*-isopropyl groups results in increasing *trans*-isomer percentage. This observation further supports the proposed steric interaction effect on geometrical isomers of amine-imine palladium complex. X-ray diffraction analysis shows that cationic palladium complex **C1** also features the methyl group *cis* to the imine and the coordinated CH$_3$CN *cis* to the amine (Figure 2). The coordination of CH$_3$CN is nonlinear (the angle of Pd-N3-C31 of 166.5^{o}), and is also bent out of the metal coordination plane because of steric interaction of CH$_3$CN with *ortho* isopropyl groups on amine-bound aniline moiety.

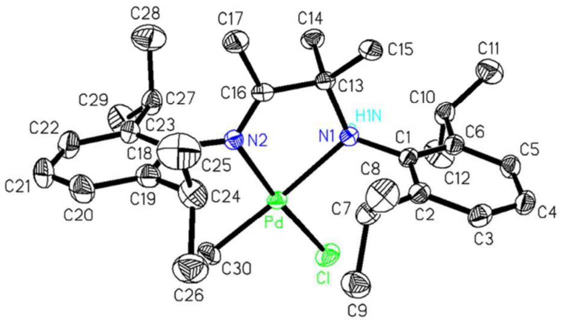


Figure 1 Molecular structure of amine-imine chloromethylpalladium complex **1**. (The hydrogens except H1N are omitted for clarity in ORTEP plot).

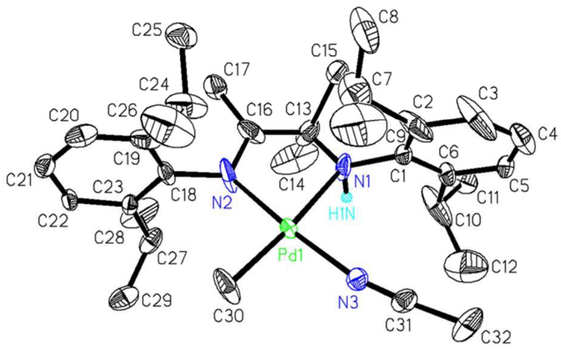


Figure 2 Molecular structure of cationic amine-imine palladium complex **C1**. (The hydrogens except H1N, BArF$^-$ anion, and 0.5H$_2$O are omitted for clarity in ORTEP plot).

Ethylene polymerization

Cationic palladium complexes **C1** and **C2** can polymerize ethylene without any cocatalysts. This is a direct proof of existence of cationic transition metal species chelating amine-imine ligand, which enable researchers to gain greater mechanistic understanding on active metal species. The polymerization results using palladium catalysts **C1** and **C2** under various conditions are summarized in Table 1.

Table 1 Ethylene polymerization results by palladium catalysts.[a]

Entry	Cat	*P* (atm)	Temp (°C)	Yield (g)	TON[b]	M_n[c]	PDI[c]	BD[d]
1	**C1**	0.5	25	0.497	1775	71.8	1.09	122
2	**C1**	5	25	0.603	2154	117.7	1.07	100
3	**C1**	20	25	0.525	1875	84.8	1.11	77
4	**C2**	0.5	25	0.148	529	19.6	1.26	125
5	**C2**	5	25	0.156	557	22.3	1.19	108
6	**C2**	20	25	0.154	550	28.5	1.08	83
7	**C1**	20	15	0.218	779	35.3	1.06	75
8	**C1**	20	35	1.677	5989	91.5	1.45	80
9	**C1**	20	45	2.122	7579	215.1	1.72	86
10	**C1**	20	55	0.923	3296	125.0	1.87	88
11	**C1**	20	65	0.434	1550	77.4	2.91	94
12	**C3**	5	25	2.927	10454	191.0	1.38	105
13	**C3**	20	55	0.382	1364	88.6	1.98	124

[a] Conditions: 10 μmol Pd catalyst, 58 mL toluene and 2 mL CH_2Cl_2, 4 h. [b] Turnover number: moles of converted ethylene per mole of Pd catalyst, (mol (E) mol^{-1} (Pd)). [c] Determined by high-temperature GPC in 1,2,4-trichlorobenzene at 150 °C, in unit of kg/mol. [d] Branching density (/1000C), determined by ^1H NMR spectroscopy in number of branches per 1000C.

Reducing steric hindrance of the amine-imine ligand by substituting of *o*-methyl groups for *o*-isopropyl groups results in decreasing turnover number (TON) of ethylene and molecular weight of polymer (entry 1 *vs* 4, 2 *vs* 5, and 3 *vs* 6). This trend suggests that bulky aniline moieties are required for amine-imine palladium catalyst to achieve high TON and high molecular weight polymer. Little variation in activity and molecular weight was observed at different ethylene pressures (0.5-20 atm) with amine-imine palladium catalysts, which is consistent with previous observation for ethylene polymerization with α-diimine palladium catalyst.[1d,9] The polymerization results using bulky palladium catalyst **C1** over the temperature range from 15 to 65 °C (entries 3, 7-11) show that TON of C1 and molecular weight of the PE reach the maximum value at 45 °C and then decrease with elevated temperature. Differently, the highest TON of α-diimine palladium **C3** for ethylene polymerization is achieved at ~30 °C (see Figure S5 in SI), which is consistent with previous report.[4a] TON of **C1** is significantly higher than the value of α-diimine palladium **C3** (3296 *vs* 1364) at high temperature of 55 °C, strongly indicating better thermal stability of amine-imine palladium **C1** than **C3**.[10] The plot of turnover frequency (TOF) versus reaction time further indicates that the amine-imine palladium catalyst **C1** is highly stable on the basis of constant TOF at 45 °C and no decay of activity occurs over a 6 h period under the adopted conditions (Figure 3).[4a,b,8a] We attribute the enhanced thermal stability of palladium catalyst **C1** to its unique amine (sp^3 N)-palladium combination fashion, which not only shows effective axially steric block, but also prohibits free rotation of the N-aryl bond, thus supressing C-H activation with alkyl groups to form palladacyclic intermediates.[10]

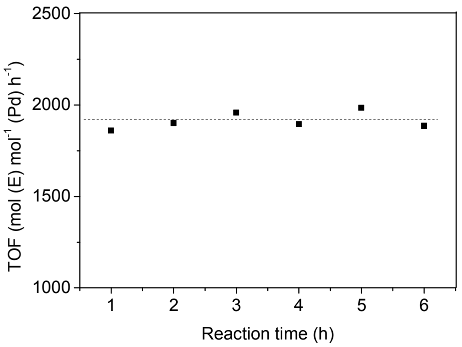
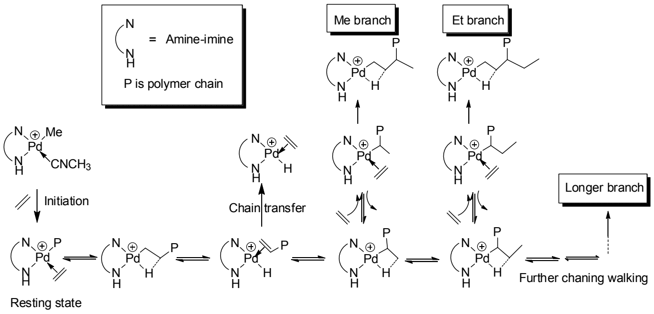


Figure 3 Plot of TOF versus reaction time in ethylene polymerization using **C1** under the conditions of 45 °C and 20 atm of ethylene pressure.

GPC analyses of the PEs obtained by **C1** and **C2** show monomodal, and narrow molecular weight distributions are observed. This result suggests a single-site palladium species for ethylene polymerization although there are two geometrical isomers (*trans*- and *cis*-isomers) in a solution of amine-imine palladium catalyst. Brookart previously presented agostic cationic α-diimine palladium is active species for ethylene polymerization, and the resting state of the catalyst is known to be the alkyl olefin complex [(α-diimine)Pd(C_2H_4)R^+].[1d,9-11] On the basis of the same observation that polymerization rate is independent of ethylene pressure, it is presumable that amine-imine palladium catalyst has similar active species and catalyst resting state for ethylene polymerization. The mechanistic model for amine-imine Pd-catalyzed ethylene polymerization and branches formation are depicted in Scheme 2.



Scheme 2 Proposed mechanism for amine-imine Pd-catalyzed ethylene polymerization.

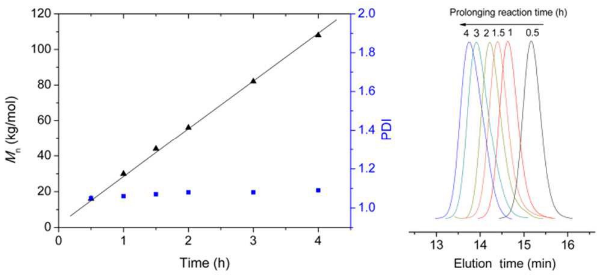


Figure 4 Plots of M_n(▲) and PDI(■) as a function of polymerization time under the condition of 25 °C and 5 atm of ethylene and GPC curves of PE samples.

The living feature of ethylene polymerizations with **C1** can be achieved below 25 °C (Table 1). PDI (M_w/M_n) values are below 1.10 and palladium black in the polymerizing mixture cannot be observed in a reaction time scale of 4 h (Figure 4), suggesting amine-imine palladium catalyst **C1** is stable and has long lifetime under the adopted conditions. To the best of our knowledge, amine-imine palladium catalyst is the second kind of palladium catalyst for living polymerization of ethylene in addition to α-diimine palladium catalyst.[1e]

The PEs produced by amine-imine palladium catalysts are also highly branched polymers (75-125/1000C) by chain walking (Scheme 2), and the branch-on-branch structures are also present, specifically a *sec*-butyl branch identified by characteritic peaks at 19.52 and 11.69 ppm (Figure S6-8 in SI) on the basis of our and Brookhart's work.[8b,9] A quantitative calculation by ^{13}C NMR spectroscopy shows that the density of *sec*-butyl branches of PE obtained by **C1** is lower than those by **C3** (2.7 *vs* 5.5/1000C, See Table S2). Branching structures of PE are also examined by its dilute solution properties. The dependency of intrinsic viscosity on polymer molecular weight detected by high-temperature gel permeation chromatography with a viscosity detector can directly reflect branch structure of the obtained PE. As shown in Figure 5, the higher intrinsic viscosity (IV) is observed for the PE obtained by **C1** while the lower value is found for the PE produced by **C3** at the same polymer molecular weight. This result suggests that the polyethylene formed by the amine-imine palladium catalyst **C1** is less branched than that obtained using a α-diimine palladium catalyst **C3**, which is substantially consistent with ^{1}H and ^{13}C NMR analysis of polymer products.

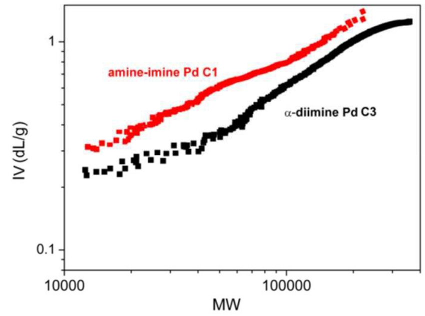


Figure 5 Intrinsic viscosity (IV) as a function of M_w for PEs obtained by amine-imine palladium **C1** and α-diimine palladium **C3** (entries 2 and 12).

Table 2 Ethylene polymerization results by palladium catalysts ^{a}.

Entry	Cat.	C_{MA} (mol/L)	T (°C)	Yield (g)	TON of E	TON of MA	MA incorp.^{b} (mol%)	M_{MA}/T_{MA}^{c} (mol%)	M_n^{d} (kg/mol)	PDI^d	BD^e (/1000C)
1	**C1**	0.1	25	0.096	332	4	1.1	64/36	15.3	1.76	91
2	**C1**	0.2	25	0.097	326	7	2.0	42/58	11.8	1.57	89
3	**C1**	0.5	25	0.116	384	10	2.5	40/60	7.3	1.46	90
4	**C1**	0.2	35	0.191	636	15	2.3	51/49	8.0	1.75	94
5	**C1**	0.2	45	0.120	392	12	3.0	49/51	4.5	1.83	99
6	**C2**	0.2	25	0.108	325	20	5.7	36/54	7.3	1.31	95
7	**C3**	0.2	25	0.861	3010	21	0.7	0/100	53.4	1.33	90

^{a} Polymerization conditions: 20 μmol catalyst, 0.5 atm of ethylene pressure, total volume 60 mL (58 mL toluene and 2 mL CH_2Cl_2), 8h. ^{b} Incorporation of MA in copolymer, which is determined by ^{1}H NMR. ^{c} Molar ratios of main chain-MA (M_{MA}, x) to terminal-MA (T_{MA}, y), which is determined by ^{1}H NMR. ^{d} Determined by high-temperature GPC in 1,2,4-trichlorobenzene at 150 ˚C. ^{e} Branching density, determined by ^{1}H NMR spectroscopy in number of branches per 1000C.

Copolymerization of ethylene and methyl acrylate (MA)

Copolymerization of ethylene with methyl acrylate (MA) can be successfully performed using amine-imine palladium catalysts (Table 2). MA incorporation in copolymer can be clearly identified by ^{1}H NMR spectroscopy of ethylene-MA (E-MA) copolymer (Figure 6). Reduction of the steric bulk of amine-imine ligand or increasing MA concentration results in higher MA incorporation but lower molecular weight of polymer. In comparison with copolymerization of ethylene and MA with α-diimine palladium catalyst **C3**, a 3-fold increase in incorporation of MA can be achieved using amine-imine palladium catalyst **C1** under the same reaction conditions although low activity is observed (entries 2 vs 7 in Table 2). Presumably, binding of the electron-deficient olefin (MA) on palladium center chelating amine-imine ligand is favorable by reducing the electrophilicity of the palladium metal center because α-diimine ligand is a stronger π-acceptor than amine-imine ligand.

The obtained E-MA copolymers are highly branched (90-99/1000C), which is similar to that obtained using α-diimine palladium catalyst.[3a] It is reported that copolymerization of ethylene with MA can usually produce a highly branched E-MA copolymer containing ester at the end of the branches using α-diimine palladium catalyst **C3**, which can also be herein confirmed (see Figure S9 in SI).[3a] However, a significant difference in the ^{1}H NMR spectra of copolymers obtained by amine-imine palladium catalyst **C1** and by α-diimine palladium catalyst **C3** is the occurrence of new resonances at 2.20-2.25 ppm (Figure 6), indicating an incorporation of acrylate units into the main chain of branched polyethylene. ^{13}C NMR spectroscopy (Figure 7) further supports the presence of direct incorporation of MA into PE main chain for amine-imine palladium catalysts in addition to incorporation of terminal acrylate unit. Carbonyl (C=O) and internal-OCH_3 resonances can be clearly observed at 177.1 and 51.4 ppm, which is different to resonance of terminal MA at 174.3 and 51.2 ppm. Carbon resonances of methylene (α_m) and methine (β_m) in main chain can be found at 45.8 and 32.5 ppm.[11] The molar ratios of main chain-MA (x) to terminal-MA (y) can be calculated by the integral of ^{1}H NMR spectroscopy. Reducing MA concentration results in an increasing main chain-MA/terminal-MA ratio (x/y). Copolymerization at low MA concentration of 0.1 M yielded a polymer with dominant main chain-MA incorporation (x/y = 64/36). The influence of temperature on x/y ratio is a result of competition of ethylene insertion rate and rearrangement rate of palladium complex.

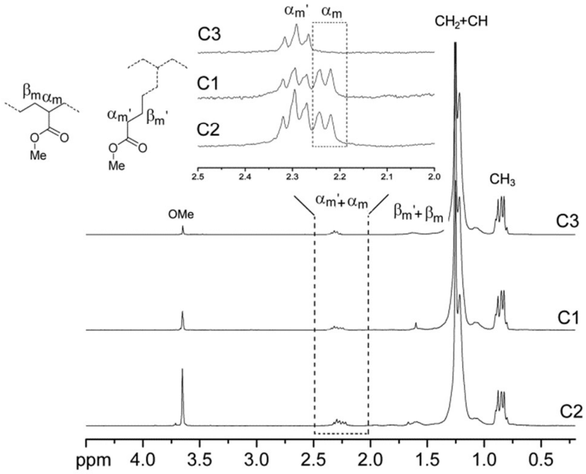


Figure 6 ^{1}H NMR spectra of E-MA copolymers produced by different palladium catalysts.

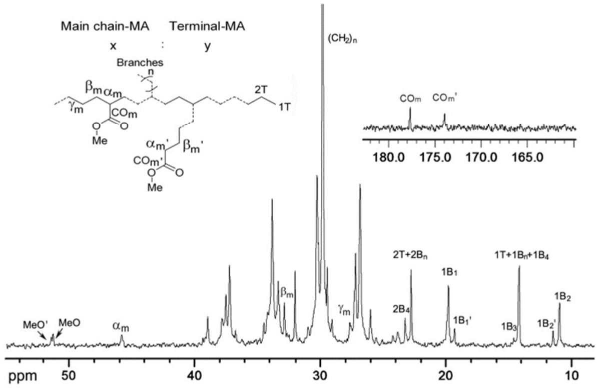
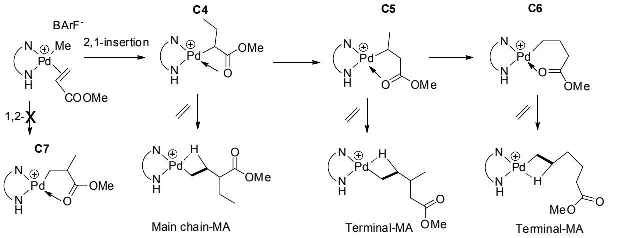


Figure 7 ^{13}C NMR spectrum of E-MA copolymer produced by catalyst **C1**.

Mechanism consideration of copolymerization

To gain insight into copolymerization mechanism, MA chelate palladium complexes were prepared by treatment of chloromethylpalladium complex **1** with sodium tetrakis (3,5-bis(trifluoromethyl)phenyl)borate (NaBArF) and MA at room temperature, and the isolated palladium complexes were studied by ^{1}H NMR analysis (Figure S10 in SI). Six-membered chelate palladium complex (**C6**) $[(\mathbf{L1})Pd(CH_2)_3C(O)OMe]^+BArF^-$ (Scheme 3) can be safely assigned, which is formed by 2,1-insertion of MA and rearrangement. Besides, 5-membered chelate palladium complex (**C5**) was formed with a ratio of 1:3 at room temperature, and trace of 4-membered chelate palladium complex **C4** was also observed based on the comparison with the previous references.[1e,12] No chelate palladium complex (**C7**) formed by 1,2-insertion of MA into the Pd-Me bond was observed. This observation suggests that insertion of MA into the Pd-Me bond occurred with predominately 2,1-regiochemistry to give 4-membered chelate palladium complex **C4**. When ethylene insertion occurs, main chain-MA unit is produced. When isomerization of 4-membered chelate palladium complex occurs prior to ethylene insertion, 5 or 6-membered chelate palladium complexes forms, which are palladium species for terminal-MA unit (Scheme 3). In comparison with MA chelate α-diimine palladium, 4- and 5-membered chelate amine-imine palladium species can be observed at elevated temperature (25 vs -60, -20 °C),[3a] which is a result of relatively slow migratory insertion of MA into amine-imine palladium. Therefore, low ethylene insertion rate and relatively slow migratory insertion of MA for amine-imine palladium are responsible for high MA incorporation and incorporation of MA into main chain together.



Scheme 3 Formation of MA chelate amine-imine palladium species (N∩NH is amine-imine ligand).

Experimental

General considerations

All manipulations involving air- and moisture- sensitive compounds were carried out under an atmosphere of dried and purified nitrogen with standard vacuum-line, Schlenk, or glovebox techniques.

Materials

2,6-Dimethylaniline and 2,6-diisopropylaniline were purchased from Aldrich Chemical and were distilled under reduced pressure before being used. TMA (1M, hexane) was purchased from Aldrich Chemical. Toluene, hexane and diethyl ether were refluxed over metallic sodium for 24 h before being used. Dichloromethane was dried over phosphorus pentoxide for 8 h, and distilled under nitrogen atmosphere. Methyl acrylate was dried over CaH_2 prior to use in polymerization. Other reagents were used as received without further purification. Amine-imine ligands **L1** and **L2**, (COD)PdMeCl and the α-diimine palladium complexes $[(2,6\text{-}^iPr_2C_6H_3\text{-}N=C(Me)\text{-}C(Me)=N\text{-}2,6\text{-}^iPr_2C_6H_3)Pd(CH_3)(CH_3CN)]^+$ $BArF^-$ (**C3**) were prepared according to literature methods.

Synthesis of $2,6\text{-}^iPr_2C_6H_3\text{-}N=C(Me)\text{-}CMe_2\text{-}NH\text{-}2,6\text{-}^iPr_2C_6H_3PdMeCl$ (1)

To a solution of L1 (0.58 g, 1.37 mmol) in dry CH_2Cl_2 (20 mL) was added 0.36 g (1.37 mmol) of (COD)PdMeCl. After stirring the mixture for 12 h at room temperature, the solution was filtered through Celite, and the solvent of the filtrate was evaporated to give a pale yellow residue. The residue was washed 3 × 10 mL hexane and dried in vacuum. The palladium complex 1 was isolated as a pale yellow solid in 56% yield. ^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm): 7.24-7.13 (m, 6H, Ar-*H*), 5.20 (s, 1H, N*H*), 4.02 (sept, 1H, C*H*(CH$_3$)$_2$), 3.34 (sept, 1H, C*H*(CH$_3$)$_2$), 3.16 (sept, 2H, C*H*(CH$_3$)$_2$), 1.89 (s, 3H, N=C-C*H*$_3$), 1.82 (s, 3H, NHC(C*H*$_3$)$_2$), 1.75 (d, 3H, CH(C*H*$_3$)$_2$), 1.43 (d, 3H, CH(C*H*$_3$)$_2$), 1.42 (d, 3H, CH(C*H*$_3$)$_2$), 1.38 (d, 3H, CH(C*H*$_3$)$_2$), 1.36 (d, 3H, CH(C*H*$_3$)$_2$), 1.35 (d, 3H, CH(C*H*$_3$)$_2$), 1.27 (d, 3H, CH(C*H*$_3$)$_2$), 1.16 (s, 3H, NHC(C*H*$_3$)$_2$), 1.11 (d, 3H, CH(C*H*$_3$)$_2$), 0.36 (s, 3H, Pd-C*H*$_3$). ^{13}C NMR (75 MHz, CDCl$_3$), δ (ppm): 190.19, 142.95, 142.42, 141.55, 138.70, 136.08, 127.00, 126.28, 124.63, 123.96, 123.68, 68.21, 30.79, 29.93, 28.65, 27.90, 27.56, 27.26, 25.19, 24.42, 23.39, 23.09, 21.13, 1.18. Anal. Calcd for $C_{30}H_{47}ClN_2Pd$: C, 62.38; H, 8.20; N, 4.85. Found: C, 62.51; H, 8.17; N, 4.80%.

Synthesis of 2,6-Me$_2$C$_6$H$_3$-N=C(Me)-CMe$_2$-NH-2,6-Me$_2$C$_6$H$_3$PdMeCl (2)

Following the above procedure, palladium complex 2 was isolated in 48% yield as pale yellow solid. ^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm): 7.19-6.91 (m, 6H, Ar-*H*), 4.83 (s, 1H, N*H*), 2.99 (s, 3H, Ar-C*H*$_3$), 2.46 (s, 3H, Ar-C*H*$_3$), 2.32 (s, 3H, Ar-C*H*$_3$), 2.22 (s, 3H, Ar-C*H*$_3$), 1.97 (s, 3H, N=C-C*H*$_3$), 1.78 (s, 3H, NHC(C*H*$_3$)$_2$), 1.22 (s, 3H, NHC(C*H*$_3$)$_2$), 0.25 (s, 3H, Pd-C*H*$_3$). ^{13}C NMR (75 MHz, CDCl$_3$), δ (ppm): 190.22, 144.01, 140.42, 130.97, 129.70, 128.66, 128.31, 127.99, 126.10, 125.11, 67.40, 32.47, 23.62, 23.53, 23.02, 19.39, 19.01, 18.53, 0.15. Anal. Calcd for $C_{22}H_{31}ClN_2Pd$: C, 56.78; H, 6.71; N, 6.02. Found: C, 56.49; H, 6.64; N, 6.00%.

Synthesis of cationic palladium complex [(2,6-^{i}Pr$_2$C$_6$H$_3$-N=C(Me)-CMe$_2$-NH-2,6-^{i}Pr$_2$C$_6$H$_3$)PdMe(NCMe)]$^+$BArF$^-$ (C1)

To a solution of complex 1 (0.44 g, 0.76 mmol) in dry CH$_2$Cl$_2$ (20 mL) was added NaBArF (0.70 g, 0.79 mmol) and CH$_3$CN (2 mL) under nitrogen atmosphere, and the reaction mixture was stirred for 24 h at room temperature. Sodium chloride was removed from the reaction mixture via filtration, yielding a clear colorless solution. The CH$_2$Cl$_2$ was removed in vacuum, and the product was precipitated by 30 mL hexane. The resulting white powder was filtered through Celite, washed with 3 × 10 mL hexane and dried in vacuum. The product C1 was isolated as a white solid in 46% yield. Isomers were observed in a ratio of 0.8:1 as determined by ^{1}H NMR spectroscopy. ^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm): *Trans*-isomer: 7.67 (s, 8H, Ar-*H* in BArF$^-$), 7.50 (s, 4H, Ar-*H* in BArF$^-$), 7.35-7.15 (m, 6H, Ar-*H*), 5.10 (s, 1H, N*H*), 3.84 (sept, 1H, C*H*(CH$_3$)$_2$), 3.04 (sept, 1H, C*H*(CH$_3$)$_2$), 2.92 (m, 2H, C*H*(CH$_3$)$_2$), 1.89 (s, 3H, N≡C-C*H*$_3$), 1.87 (s, 3H, NHC(C*H*$_3$)$_2$), 1.81 (s, 3H, NHC(C*H*$_3$)$_2$), 1.59 (d, 3H, NHC(C*H*$_3$)$_2$), 1.42 (d, 3H, CH(C*H*$_3$)$_2$), 1.36-1.17 (m, 18H, CH(C*H*$_3$)$_2$), 1.10 (d, 3H, CH(C*H*$_3$)$_2$), 0.41 (s, 3H, Pd-C*H*$_3$). *Cis*-isomer: 7.67 (s, 8H, Ar-*H* in BArF$^-$), 7.50 (s, 4H, Ar-*H* in BArF$^-$), 7.35-7.15 (m, 6H, Ar-*H*), 5.99 (s, 1H, N*H*), 3.98 (sept, 1H, C*H*(CH$_3$)$_2$), 3.14 (sept, 1H, C*H*(CH$_3$)$_2$), 2.92 (m, 2H, C*H*(CH$_3$)$_2$), 1.88 (s, 3H, N≡C-C*H*$_3$), 1.86 (s, 3H, N=C-C*H*$_3$),1.65 (s, 3H, NHC(C*H*$_3$)$_2$), 1.53 (d, 3H, NHC(C*H*$_3$)$_2$), 1.43 (d, 3H, CH(C*H*$_3$)$_2$), 1.36-1.17 (m, 18H, C*H*$_3$), 1.11 (d, 3H, CH(C*H*$_3$)$_2$), 0.23 (s, 3H, Pd-C*H*$_3$). ^{13}C NMR (75 MHz, CDCl$_3$), δ (ppm): 195.19, (*C*=N for *trans*-isomer), 185.65 (*C*=N for *cis*-isomer), 162.60, 161.94, 161.28, 160.62, 143.01, 142.37, 141.46, 141.28, 140.21, 139.91, 138.67, 138.50, 134.75, 129.93, 129.50, 129.11, 128.67, 128.45, 128.28, 127.83, 127.59, 126.32, 126.14, 124.78, 124.65, 124.48, 124.36, 124.22, 122.72, 120.75, 119.12, 117.45, 69.54, 31.14, 30.32, 30.22, 29.03, 28.81, 28.54, 28.43, 28.30, 28.07, 27.39, 25.64, 24.81, 24.37, 24.17, 23.94, 23.80, 23.73, 23.37, 23.19, 23.01, 22.90, 21.56, 19.63, 6.71, 2.07, 1.41 (Pd-*C*H$_3$ for *trans*-isomer), -1.40 (Pd-*C*H$_3$ for *cis*-isomer). Anal. Calcd for $C_{64}H_{62}BF_{24}N_3Pd$: C, 53.15; H, 4.32; N, 2.91. Found: C, 53.31; H, 4.39; N, 2.83%.

Synthesis of cationic palladium complex [(2,6-Me$_2$C$_6$H$_3$-N=C(Me)-CMe$_2$-NH-2,6-Me$_2$C$_6$H$_3$)PdMe(NCMe)]$^+$BArF$^-$ (C2)

Following the above procedure, C2 was isolated in 51% yield as yellow solid. Isomers were observed in 1.8:1 ratio as determined by ^{1}H NMR spectroscopy. ^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm): *Trans*-isomer: 7.68 (s, 8H, Ar-*H* in BArF$^-$), 7.50 (s, 4H, Ar-*H* in BArF$^-$), 7.12-6.98 (m, 6H, Ar-*H*), 4.65 (s, 1H, N*H*), 2.95 (s, 3H, Ar-C*H*$_3$), 2.30 (s, 3H, Ar-C*H*$_3$), 2.18 (s, 3H, Ar-C*H*$_3$), 2.10 (s, 3H, Ar-C*H*$_3$), 1.81 (s, 3H, Pd-CN-C*H*$_3$), 1.80 (s, 6H, N=C-C*H*$_3$ and one of NHC(C*H*$_3$)$_2$), 1.27 (s, 3H, NHC(C*H*$_3$)$_2$), 0.24 (s, 3H, Pd-C*H*$_3$); *Cis*-isomer: 7.68 (s, 8H, Ar-*H* in BArF$^-$), 7.50 (s, 4H, Ar-*H* in BArF$^-$), 7.12-6.98 (m, 6H, Ar-*H*), 5.49 (s, 1H, N*H*), 2.94 (s, 3H, Ar-C*H*$_3$), 2.37 (s, 3H, Ar-C*H*$_3$), 2.23 (s, 3H, Ar-C*H*$_3$), 2.16 (s, 3H, Ar-C*H*$_3$), 1.88 (s, 3H, Pd-CN-C*H*$_3$), 1.80 (s, 6H, N=C-C*H*$_3$ and one of NHC(C*H*$_3$)$_2$), 1.17 (s, 3H, NHC(C*H*$_3$)$_2$), 0.15 (s, 3H, Pd-C*H*$_3$).^{13}C NMR (75 MHz, CDCl$_3$), δ (ppm): 194.51(*C*=N for *trans*-isomer), 184.77(*C*=N for *cis*-isomer), 162.64, 161.98, 161.32, 160.66, 143.03, 142.95, 139.08, 138.72, 134.79, 131.58, 131.14, 131.04, 130.18, 129.97, 129.58, 129.41, 129.18, 128.77, 128.36, 128.05, 127.79, 127.56, 126.86, 126.65, 126.37, 122.76, 120.68, 119.16, 117.47, 69.24, 31.82, 31.67, 23.58, 23.26, 22.54, 22.42, 19.46, 19.04, 18.79, 18.33, 18.09, 17.96, 5.27, 1.77, 1.38 (Pd-*C*H$_3$ for *trans*-isomer), -3.38(Pd-*C*H$_3$ for *cis*-isomer). Anal. Calcd for $C_{56}H_{46}BF_{24}N_3Pd$: C, 50.41; H, 3.48; N, 3.15. Found: C, 50.16; H, 3.40; N, 3.05%.

Characterizations

Elemental analyses were performed with a Vario EL series elemental analyzer from Elementar. The NMR data of complexes were obtained on a Varian Mercury-Plus 300 MHz spectrometer at ambient temperature in CDCl$_3$ using TMS as a reference. ^{1}H NMR and ^{13}C NMR spectra of polymers were carried out on a Varian Mercury-puls 500 MHz spectrometer in *o*-C$_6$D$_4$Cl$_2$. The spectra of the quantitative ^{13}C NMR were taken with a 70° flip angle, a relaxation delay of 4 s, an acquisition time of 1.5 s, and inverse gated decoupling. The total branching density (*BD*) per 1000 carbon atoms of polyethylene was determined by integrating methyl proton signals with respect to signals of all protons in ^{1}H NMR spectrum. Gel permeation chromatography (GPC) analyses of the molecular weight and molecular weight distribution (PDI = M_w/M_n) of the polymers at 150 °C were performed on a high-temperature chromatography, PL-GPC 220 instrument equipped with a triple detection array, including a differential refractive index (RI) detector, a two-angle light scattering (LS) detector, and a four-bridge capillary viscometer. The detection angles of the LS detector were 15 and 90, and the laser wavelength was 658 nm. 1,2,4-Trichlorobenzene (TCB) was used as the eluent at a flow rate of 1.0 mL/min.

Crystal Structure Determination

The X-ray diffraction data of single crystals were obtained with the ω-2θ scan mode on a Bruker SMART 1000 CCD diffractiometer with graphite-monochromated Mo Kα radiation (λ = 0.71073). The structure was solved using direct methods, and further refinement with full-matrix least squares on F^2 was obtained with the SHELXTL program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

Polymerization of Ethylene

Except for ethylene polymerization at 0.5 atm performed in a round-bottom Schlenk flask with stirring bar, the other polymerization reactions were carried out in a Parr reactor. A mechanically stirred 100 mL Parr reactor was heated to 150 °C for 2 h under vacuum and then cooled to room temperature. The autoclave was pressurized with ethylene and vented three times. The autoclave was then charged with 58 mL toluene at initialization temperature. The system was maintained by continuously stirring for 5 min, and then 2 mL solution of palladium complex in CH_2Cl_2 was charged into the autoclave. The ethylene pressure was raised to the specified value, and the reaction was carried out for a certain time. Polymerization was terminated by addition of triethylsilane after releasing ethylene pressure. The solvents were removed on a rotary evaporator. The obtained polymer was dissolved in hexane and filtered through a plug of silica gel to remove palladium black before precipitating in methanol. The resulting precipitated polymers were collected and treated by filtering, washing with methanol several times, and drying under vacuum at 40 °C to a constant weight.

Copolymerization of Ethylene and MA

In a typical procedure, a 100 mL round-bottom Schlenk flask with stirring bar was heated 3 h to 150 °C under vacuum and then cooled to room temperature. The flask was pressurized to 1 atm of ethylene and vented three times. The appropriate toluene solvent and polar monomers (MA) were introduced into the glass reactor under ethylene atmosphere at 25 °C. The system was maintained by continuously stirring for 10 min, and then 2 mL solution of palladium catalyst (20 μmol) in CH_2Cl_2 were syringed into the well-stirred solution, and the total reaction volume was kept at 60 mL. The ethylene pressure was kept constant value of 0.5 atm by continuous feeding of gaseous ethylene throughout the reaction. The polymerizations were terminated by the addition of a large amount of methanol after continuously stirring for a certain time. Then the methanol was decanted off, the sticky polymer was redissolved in petroleum ether. The polymer solution was filtered through alumina and silica to remove catalyst residues. The resulting precipitated polymers were collected and treated by concentration, and drying in vacuum at 40 °C to a constant weight. The incorporation (mol%) of MA was calculated from ^{1}H NMR analysis.

Conclusions

In summary, we successfully developed a new kind of thermally stable amine-imine palladium catalyst that can polymerize ethylene to produce highly branched polymer. The better thermal stability up to 45 °C and living polymerization of ethylene at elevated temperature of 25 °C are observed relative to α-diimine palladium catalyst. Copolymerization of ethylene and MA using amine-imine palladium catalysts afforded branched polymers with a higher incorporation of MA relative to those obtained by α-diimine palladium catalyst. Both direct incorporation of an acrylate unit into main chain and migratory incorporation of terminal acrylate unit can occur in amine-imine palladium catalyzed copolymerization. Incorporation of polar monomers in polyethylene main chain become possible using amine-imine palladium catalyst by changing imine-Pd to amine-Pd combination mode, and synthesis of functional polyethylene by copolymerization of ethylene with polar monomers is ongoing.

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Graphic Abstract

Amine-Imine Palladium Catalysts for Living Polymerization of Ethylene and Copolymerization of Ethylene with Methyl Acrylate: Incorporation of Acrylate Units into Main Chain and Branch End

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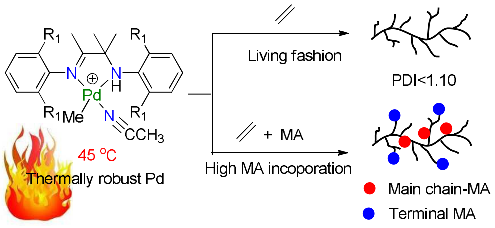

A bulky amine-imine palladium catalyst is thermally stable at 45 °C and can catalyze ethylene polymerization in a living fashion at 25 °C. Copolymerizations of ethylene and methyl acrylate (MA) afford branched ethylene-MA copolymers with terminal and main chain acrylate units.