ACS Catalysis
Research Article
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Ethylene Polymerization and Copolymerization with Polar Monomers by Cationic Phosphine Phosphonic Amide Palladium Complexes

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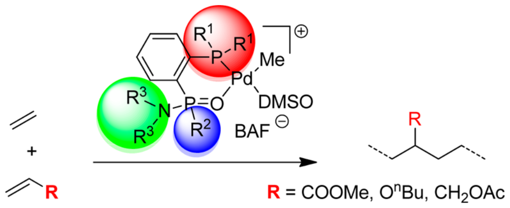
Ⓢ *Supporting Information*

ABSTRACT: The synthesis, characterization, and olefin (co)-polymerization studies of a series of palladium complexes bearing phosphine phosphonic amide ligands were investigated. In this ligand framework, substituents on three positions could be modulated independently, which distinguishes this class of ligand and provides a great deal of flexibilities and opportunities to tune the catalytic properties. The palladium complex with an *o*-MeO-Ph substituent on phosphine is one of the most active palladium catalysts in ethylene polymerization, with 1 order of magnitude higher activity than the corresponding classic phosphine-sulfonate palladium complex. Meanwhile, the polyethylene generated by this new palladium complex showed ca. 6 times higher molecular weight in comparison to that by the classic phosphine-sulfonate palladium complex. In ethylene/methyl acrylate copolymerization, the new palladium complex showed lower activity, generating copolymer with similar methyl acrylate incorporation and much higher molecular weight. The new palladium complex was also able to copolymerize ethylene with other polar monomers, including butyl vinyl ether and allyl acetate, making it one of the very few catalyst systems that can copolymerize ethylene with multiple industrially relevant polar monomers.



KEYWORDS: *olefin polymerization, palladium, phosphine ligands, copolymerization, polar monomer*

■ INTRODUCTION

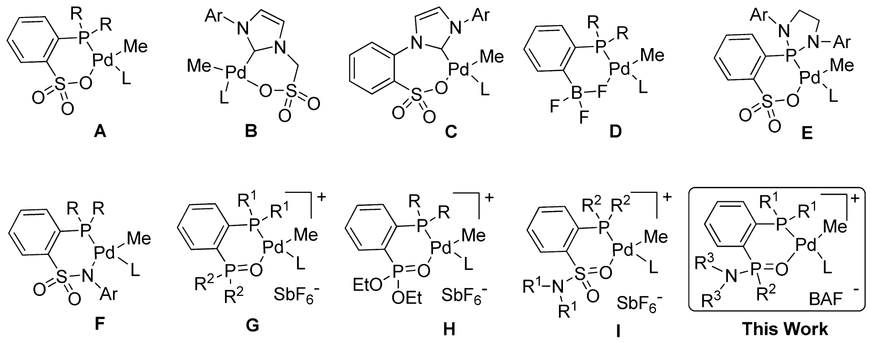
Since the seminal discovery of α-diimine Ni(II) and Pd(II) catalysts by Brookhart and phenoxyminato Ni(II) catalysts by Grubbs, late-transition-metal-mediated olefin polymerization and copolymerization with polar functionalized monomers have attracted continuing attention.[1−3] Both catalyst systems possessed some limitations in polar monomer copolymerization. Phenoxyminato Ni(II) catalysts were mainly applied for the copolymerization of ethylene with polar functionalized norbornene monomers. Pd(II) α-diimine catalysts could be used in ethylene copolymerization with acrylates, vinyl ketones, vinyl ethers, and a few other polar monomers, affording totally amorphous copolymers with polar groups located mainly at the ends of branches.[2] Recently, we reported that Pd(II) α-diimine complexes bearing a benzhydryl moiety were highly active in ethylene/methyl acrylate copolymerization, generating semicrystalline copolymer with high molecular weight and very low branching density.[2p] Neutral Pd(II) alkyl complexes containing phosphine-sulfonate ligands (**A**, Chart 1) have emerged as highly promising catalysts for olefin/polar vinyl monomer copolymerization. These catalysts are capable of copolymerizing ethylene with a surprisingly wide variety of polar monomers to afford functionalized linear copolymers.[4] The most distinguishing feature of this class of ligand is the combination of a very strongly σ donating phosphine moiety and a very weakly σ donating sulfonate moiety. It is generally believed that this electronically nonsymmetric ligand framework can efficiently inhibit β-H (X) elimination, therefore producing linear polymers and enabling the polar monomer incorporation during ethylene polymerization.[4,5]

Since these initial reports, there have been numerous studies on the modifications of the ligand structure. Several anionic bidentate ligands with nonsymmetric frameworks and the corresponding neutral palladium complexes have been designed and synthesized. For example, Nozaki et al. replaced the phosphine moiety with the more σ donating N-heterocyclic carbene (NHC) group and prepared the neutral NHC-sulfonate palladium complexes (**B**, Chart 1).[6] Jordan et al. described the synthesis of a similar arene bridging NHC-sulfonate palladium complex (**C**, Chart 1).[7] Unfortunately, neither complex was active for ethylene polymerization. Jordan and Piers independently reported the synthesis and characterization of bidentate trifluoroborate-phosphine palladium complexes (**D**, Chart 1), which were only capable of dimerizing ethylene to butenes at low activities.[8] Mecking et al. showed that the diazaphospholidine-sulfonatopalladium(II) complexes (**E**, Chart 1) could not incorporate any methyl acrylate (MA) unit in E-MA copolymerization.[9] Recently, the same group

Received: July 15, 2015
Revised: August 28, 2015
Published: September 1, 2015

DOI: 10.1021/acscatal.5b01490
ACS Catal. 2015, 5, 5932−5937

Chart 1. Bidentate Neutral and Cationic Pd(II) Catalysts with Nonsymmetric Ligand Structures



studied the ethylene oligomerization behavior of some neutral phosphine-sulfonamide palladium(II) complexes (**F**, Chart 1).[10] Interestingly, very little success was achieved using these anionic ligands. These palladium complexes were only capable of ethylene homopolymerization (**E**) and ethylene oligomerization (**D** and **F**) or showed no activity toward ethylene (**B** and **C**).

In contrast to these anionic ligands, some exciting results came from electronically nonsymmetric neutral ligands and the corresponding cationic palladium catalysts. For example, Nozaki et al. showed that the cationic bis-phosphine monoxide palladium complexes (**G**, Chart 1) were highly active for ethylene polymerization (activity up to 2800 kg mol^{-1} h^{-1}). These complexes could also copolymerize ethylene with a number of challenging polar monomers to afford highly linear functionalized polymers.[11] This study represented a significant advance in the field by providing a second catalyst system that can copolymerize ethylene with a series of industrially relevant polar monomers. Recently, Jordan et al. showed that cationic palladium catalysts containing phosphine-diethyl phosphonate ligands (**H**, Chart 1) were highly active in ethylene polymerization (activity up to 2640 kg mol^{-1} h^{-1}).[12] These complexes could copolymerize ethylene with MA and acrylic acid at greatly reduced activity (1.2–150 kg mol^{-1} h^{-1}) with 0.45–2.6% of polar monomer incorporation. Recently, we showed that cationic palladium complexes bearing phosphine-sulfonamide ligands (**I**, Chart 1) could oligomerize ethylene at moderate activity to generate α-olefin with high selectivity.[13]

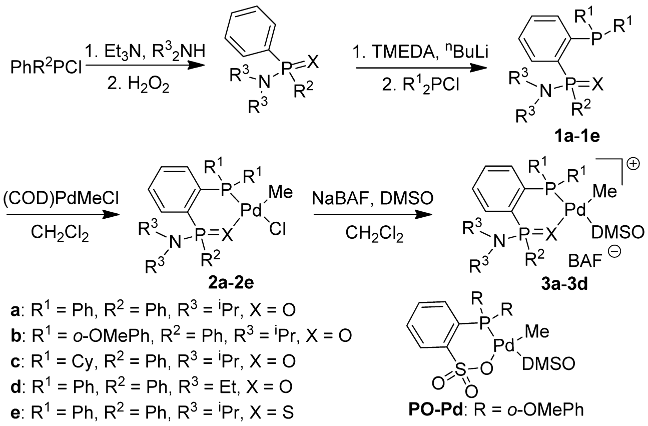
In this contribution, we report the synthesis, ethylene polymerization, and ethylene/polar monomer copolymerization studies of a series of cationic palladium complexes bearing phosphine phosphonic amide ancillary ligands. These palladium complexes showed greatly enhanced catalytic activity and polymer molecular weight in ethylene homopolymerization in comparison with classic phosphine-sulfonate complexes (**A**, Chart 1). In addition, they were capable of copolymerizing ethylene with a series of polar monomers, including MA, butyl vinyl ether (BVE), and allyl acetate (AA), with good activity, good polar monomer incorporation, and great copolymer molecular weight.

The phosphonic amide group was expected to be a weak donor, thus resembling the electronically nonsymmetric feature of the classic phosphine-sulfonate ligands. In this ligand framework, the substituents on three positions could be modified independently, providing a great deal of flexibility to tune the catalytic properties of these palladium complexes. In classic phosphine-sulfonate palladium complexes, the substituents on phosphine affect the steric and electronic properties of the palladium center and correspondingly the polymerization properties.[14] In this new ligand structure, the substituents on phosphine oxide and nitrogen atom could exert additional control on the electronic properties of the palladium center. Moreover, these substituents offer steric influence over the weak σ-donor side of the ligand framework, which could not be realized in the classic phosphine-sulfonate system.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Palladium Complexes. The phosphine phosphonic amide ligands were previously synthesized and used as supporting ligands for palladium-catalyzed Suzuki–Miyaura cross-coupling reactions.[15] However, the palladium complexes based on these ligands have never been isolated or studied in ethylene (co)polymerization. In this study, ligands **1a–e** were prepared using literature procedures.[15] Subsequently, the neutral chloro methyl palladium complexes **2a–e** were prepared in high yields from the reaction of ligands **1a–e** with 1 equiv of (COD)-PdMeCl (Scheme 1). The reaction of complexes **2a–e** with 1 equiv of sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (NaBAF) in the presence of DMSO led to the formation of cationic palladium complexes **3a–d** in 58–67% yields. The palladium complexes **2a–e** and **3a–d** were characterized by ^{1}H, ^{13}C, and ^{31}P NMR, elemental analysis, and mass spectrometry.

Scheme 1. Synthesis of the Phosphine Phosphonic Amide Ligands and the Palladium Complexes



a: R^1 = Ph, R^2 = Ph, R^3 = ^{i}Pr, X = O
b: R^1 = *o*-OMePh, R^2 = Ph, R^3 = ^{i}Pr, X = O
c: R^1 = Cy, R^2 = Ph, R^3 = ^{i}Pr, X = O
d: R^1 = Ph, R^2 = Ph, R^3 = Et, X = O
e: R^1 = Ph, R^2 = Ph, R^3 = ^{i}Pr, X = S

The molecular structures of **2a**,**e** were determined by X-ray diffraction analysis (Figures 1 and 2). In both cases, the geometry at the palladium center is square planar with the methyl substituent cis to the coordinating phosphine atom. The six-membered (PO)Pd or (PS)Pd chelate ring adopts a

DOI: 10.1021/acscatal.5b01490
ACS Catal. 2015, 5, 5932–5937

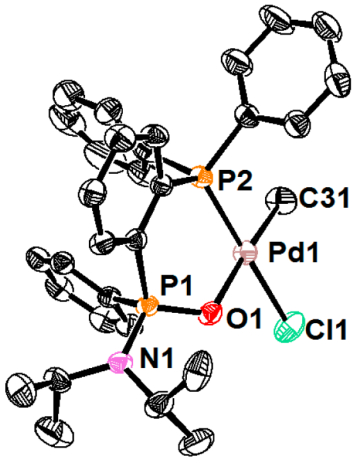


Figure 1. Molecular structure of **2a**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Pd1−C31 2.068(8), Pd1−O1 2.194(5), Pd1−P2 2.219(2), Pd1−Cl1 2.370(2), P1−O1 1.499(5), P1−N1 1.636(5); C31−Pd1−O1 176.3(4), C31−Pd1−P2 86.7(3), O1−Pd1−P2 95.95(14), C31−Pd1−Cl1 88.9(3), O1−Pd1−Cl1 88.68(15), P2−Pd1−Cl1 174.24(10), O1−P1−N1 111.2(3).

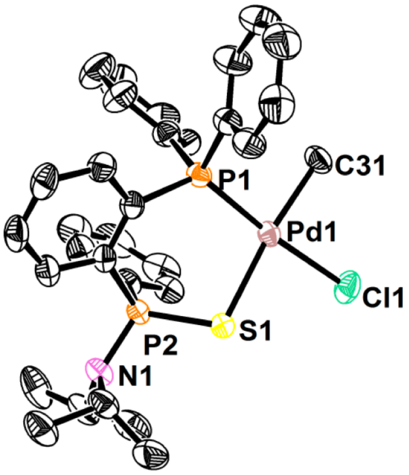


Figure 2. Molecular structure of **2e**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Pd1−C31 2.089(4), Pd1−P1 2.2136(13), Pd1−Cl1 2.3774(15), Pd1−S1 2.3895(11), S1−P2 1.9888(17), P2−N1 1.651(4); C31−Pd1−P1 87.20(14), C31−Pd1−Cl1 87.15(14), P1−Pd1−Cl1 174.30(4), C31−Pd1−S1 173.48(15), P1−Pd1−S1 98.50(5), Cl1−Pd1−S1 87.18(5).

puckered conformation, with one P-Ph substituent occupying a pseudoaxial position and the other a pseudoequatorial position. The Pd−Me bond length in complex **2a** (2.068 Å) is slightly shorter than that in complex **2e** (2.089 Å), suggesting a more electronically deficient palladium center in complex **2a**. On comparison of the crystallographic data for a series of (P,O)Pd(Me)(Cl) complexes, the palladium−methyl bond in the bisphosphine monoxide palladium complex **G** (Chart 1) appeared to be the longest (2.066 Å in comparison with 2.023−2.052 Å in the rest).[4d] This demonstrated the strongest trans influence of the phosphine oxide moiety to the palladium−methyl bond in complex **G**, which might be responsible for its high activity in ethylene polymerization and copolymerization. In complex **2a**, the palladium−methyl bond distance (2.068 Å) is similar to that in complex **G**, suggesting a similarly strong trans influence of the phosphonic amide moiety.

Ethylene Polymerization Studies. First, an in situ activation procedure was employed to evaluate the catalytic properties of the neutral palladium complexes **2a**−**c**. The ethylene polymerization was initiated by addition of 1.2 equiv of $AgSbF_6$. Complex **2b** with an *o*-Me-Ph substituent showed activity much higher than that of complexes **2a**,**c** (Table 1, entries 1−3). In addition, complex **2b** afforded polyethylene with molecular weight much higher than that by complexes **2a**,**c**. When the activator was changed from $AgSbF_6$ to sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (NaBAF), the activity of **2b** increased from 7.0×10^6 to 8.5×10^6 g mol^{-1} h^{-1} (Table 1, entry 2 versus entry 4). Meanwhile, the polyethylene molecular weight (M_n) increased from 3.7×10^4 to 4.1×10^4. The sulfur-containing complex **2e** was not active at all in ethylene polymerization with the addition of $AgSbF_6$ or NaBAF (Table 1, entry 5).

Subsequently, the DMSO-coordinated single-component palladium complexes **3a**−**d** were studied. Generally, the catalytic activity slightly decreased (Table 1, entries 6−8), which was probably due to the coordinating effect of DMSO. However, the molecular weight of the polyethylene increased. Specifically for complex **3b**, the molecular weight (M_n) increased to 13×10^4 from that of **2b** (4.1×10^4). Complex **3d** with an Et_2N substituent showed very low activity and generated polyethylene with very low molecular weight (Table 1, entry 9). This suggested that the steric effect of the substituent on the N atom was crucial to obtain high-performance catalysts, which provided a promising direction for future modifications on this class of ligand.

These catalysts showed interesting time dependence properties in ethylene polymerization. For classic phosphine-sulfonate palladium catalysts, the polymer molecular weight could only be slightly increased at longer polymerization time.[16] For complex **3b**, the molecular weight (M_n) increased from 5.8×10^4 to 13×10^4 and 19×10^4, when the polymerization time was increased from 10 to 30 min and 1 h, respectively (Table 1, entries 7, 10, and 11). Meanwhile, the polymer yield was also increased along with polymerization time. The increase after 30 min became minimal, which was probably due to the significant precipitation of polyethylene after 20 min (Table 1, entries 10 and 11). To probe the lifetime of catalyst **3b**, kinetic studies at 100 °C were carried out. The polymer molecular weight was low at 100 °C (see below), therefore preventing mass transport effects to some extent (Figure 3 and Table S1 in the Supporting Information). When 0.8 μmol of **3b** was used, the polymer yield increased approximately linearly with time within 2 h, at which point the magnetic stir bar completely stopped. When the catalyst loading was decreased to 0.2 μmol, the polymer yield increased approximately linearly with time within 2 h. At about 2.5 h, a transparent polymer shell formed on top of the solution, which may prevent ethylene from getting through to the catalyst solution. Nevertheless, no palladium black was observed for any of the polymerization runs and the lifetime of complex **3b** should be longer than 2 h at 100 °C.

The influence of temperature on ethylene polymerization was also investigated. When the polymerization temperature was increased to 100 °C, the activity of complex **3b** increased more than 2 times to 1.34×10^7 g mol^{-1} h^{-1} (Table 1, entry 12), making it one of the most active palladium catalysts for ethylene homopolymerization. However, the molecular weight (M_n) was significantly reduced to 1.3×10^4, suggesting greatly enhanced chain transfer at this temperature. When the temperature was decreased to 60, 40, and 20 °C, the activity

DOI: 10.1021/acscatal.5b01490
ACS Catal. 2015, 5, 5932−5937

Table 1. Ethylene Homopolymerization with the Palladium Complexes

entry[a]	cat.	[cat.] (μmol)	T (°C)	t (h)	yield (g)	act.[b]	M_n[c] (10^4)	PDI[c]	T_m[d] (°C)
1	**2a**[e]	1	80	0.5	0.08	1.6	0.11	2.13	118.2
2	**2b**[e,f]	1	80	0.5	3.50	70	3.7	3.33	129.8
3	**2c**[e]	1	80	0.5	0.75	15	0.29	2.33	126.7
4	**2b**[f,g]	1	80	0.5	4.26	85	4.1	3.14	128.4
5	**2e**[e,g]	1	80	0.5	0	0			
6	**3a**	1	80	0.5	0.07	1.4	0.45	1.84	119.7
7	**3b**[f]	1	80	0.5	3.0	60	13	2.20	132.7
8	**3c**	1	80	0.5	0.6	12	0.66	2.13	130.0
9	**3d**	1	80	0.5	0.03	0.6	0.11	1.36	113.0
10	**3b**	1	80	0.16	1.1	66	5.8	2.25	128.9
11	**3b**[f]	1	80	1	3.5	35	19	2.20	134.2
12	**3b**	1	100	0.5	6.7	134	1.6	3.80	123.7
13	**3b**	1	60	0.5	0.26	5.2	12	1.78	135.1
14	**3b**	1	40	0.5	0.06	1.2	5.2	1.44	135.0
15	**3b**	1	20	0.5	0.01	0.2	4.6	1.20	135.6
16	**3b**	10	20	12	1.1	0.092	10	2.01	136.6
17	**3c**	10	20	12	0.9	0.075	1.1	2.21	132.9
18	***PO-Pd***	10	20	12	0	0			
19	**PO-Pd**	1	60	0.5	0.02	0.4			136.5
20	**PO-Pd**	1	80	0.5	0.3	6	2.0	1.96	132.9
21	**PO-Pd**	1	100	0.5	0.62	12	1.5	2.01	132.7

[a]Polymerization conditions: 48 mL of toluene, 2 mL of dichloromethane, 9 atm. [b]Activity in units of 10^5 g mol^{-1} h^{-1}. [c]Determined by GPC, calibrated with polystyrene standards. [d]Determined by differential scanning calorimetry, second heating. [e]Addition of 1.2 equiv of $AgSbF_6$. [f]Significant polymer precipitation was observed after ca. 20 min. [g]Addition of 1.2 equiv of NaBAF.

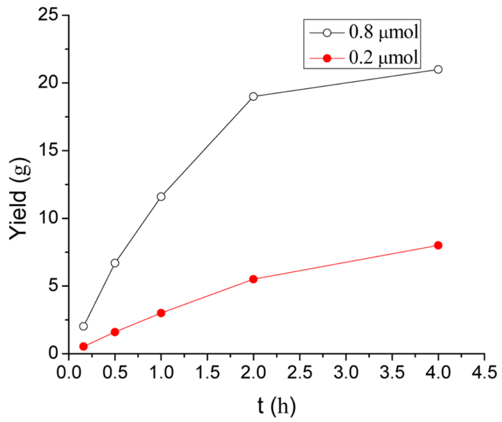


Figure 3. Plot of polymer yield versus time for complex **3b** at 100 °C, with 0.8 and 0.2 μmol catalyst loading.

decreased dramatically, with slightly decreased polymer molecular weight (Table 1, entries 13−15). After longer polymerization times at room temperature, complex **3b** could generate an appreciable amount of polyethylene with very high molecular weight (Table 1, entry 16). Similar results were observed for complex **3c** (Table 1, entry 17).

The good catalytic activity at low temperatures represented a great advantage over classic phosphine-sulfonate palladium catalysts (**PO-Pd** for example), which showed minimal activity at room temperature or 40 or 60 °C (Table 1, entries 18 and 19).[17] At 80 °C, the activity of complex **3b** (6.0×10^6 g mol^{-1} h^{-1}, Table 1, entry 7) was 10 times higher than that of complex **PO-Pd** (6.0×10^5 g mol^{-1} h^{-1}, Table 1, entry 20). At this temperature, the molecular weight of polyethylene generated by **3b** ($M_n = 13 \times 10^4$) was ca. 6 times higher than that by complex **PO-Pd** ($M_n = 2.0 \times 10^4$). At 100 °C, the activity difference became even more dramatic, while the difference between polyethylene molecular weights became smaller (Table 1, entry 12 versus entry 21). The branching density of the polyethylene generated by **3b** (Table 1, entry 7, 7.2 branches/1000C; calculated on the basis of ^{1}H NMR, Figure S31 in the Supporting Information) was similar to that by **PO-Pd** (Table 1, entry 20, 9 branches/1000C; Figure S32 in the Supporting Information). The microstructure analysis using ^{1}H NMR presented some interesting results. In the ^{1}H NMR spectrum of the polyethylene generated by classic phosphine-sulfonate palladium catalysts (**PO-Pd** for example, Figure S32),[16] resonances from terminal and internal double bonds could be clearly observed. However, in the ^{1}H NMR spectrum of the polyethylene generated by **3b**, the resonances from double bonds could hardly be observed (Figure S31). The greatly enhanced polyethylene molecular weight by **3b** might be the reason for this difference.

Ethylene/Polar Monomer Copolymerization Studies. Complex **3b** demonstrated great properties in E-MA copolymerization. Butylated hydroxytoluene (BHT) was added as a radical polymerization inhibitor for all of the E-MA copolymerization runs. At 9 atm of ethylene pressure and room temperature, **3b** showed appreciable catalytic activity, generating copolymer with high molecular weight ($M_n = 2.6 \times 10^4$, Table 2, entry 1). Again, this could not be realized using classic phosphine-sulfonate palladium catalysts. When the temperature was increased to 80 °C, the activity increased dramatically to 6.0×10^3 g mol^{-1} h^{-1}, with high copolymer molecular weight (Table 2, entry 2). When the temperature was increased from 80 to 100 °C, the catalytic activity greatly increased at the expense of polyethylene molecular weight, due to faster chain transfer in ethylene homopolymerization (Table 1, entry 6 versus entry 11). In contrast, the catalytic activity was greatly increased, with greatly increased copolymer molecular weight in E-MA copolymerization (Table 2, entry 2 versus entry 3). Probably, the chain transfer process was not sensitive

DOI: 10.1021/acscatal.5b01490
ACS Catal. 2015, 5, 5932−5937

Table 2. Ethylene/Polar Monomer Copolymerization by the Palladium Complexes

entry[a]	cat.	monomer	P (atm)	[monomer] (M)	T (°C)	t (h)	incorp[b] (%)	yield (mg)	act.[c]	M_n[d] (10^3)	PDI[d]
1	**3b**	MA	9	1	20	12	2.3	140	0.6	26	1.97
2	**3b**	MA	9	1	80	1	3.2	120	6.0	18	1.47
3	**3b**	MA	9	1	100	1	7.1	277	14	32	1.66
4	**3b**	MA	9	3	100	1	33	130	6.5	12	1.37
5	**3b**	MA	5	1	100	1	16	174	8.7	27	1.92
6	**3c**	MA	9	1	100	1	3.2	40	2.0	2.3	1.93
7	**3b**	BVE	9	1	80	12	0.4	400	1.7	13	1.82
8	**3b**	BVE	5	1	80	12	2.2	100	0.4	3.2	3.98
9	**3b**	AA	9	1	80	12	0.5	640	2.7	5.8	2.22
10	**3b**	AA	5	1	80	12	2.8	120	0.5	2.5	3.53
11	**PO-Pd**	MA	9	1	20	12		0	0		
12	**PO-Pd**	MA	9	1	100	1	10	600	30	11	2.08
13	**PO-Pd**	MA	9	3	100	1	40	300	15	4.4	2.63
14	**PO-Pd**	MA	5	1	100	1	17	500	25	4.5	2.39

[a] Conditions: total volume of toluene and polar vinyl monomer 50 mL (200 mg of BHT for MA, 30 μL of 2,6-di-*tert*-butylpyridine for *n*-butyl vinyl ether), 20 μmol of catalyst, 1 h. [b] Determined by ^{1}H NMR spectroscopy. [c] Activity in units of 10^3 g mol^{-1} h^{-1}. [d] Determined by GPC, calibrated with polystyrene standards.

to temperature in E-MA copolymerization. When the MA concentration was increased to 3 mol/L, MA incorporation was increased to 33% at the expense of copolymer molecular weight ($M_n = 1.2 \times 10^4$, Table 2, entry 4). When the ethylene pressure dropped to 5 atm, MA incorporation increased to 16% with only slightly decreased copolymer molecular weight ($M_n = 2.7 \times 10^4$, Table 2, entry 5).

In comparison with **3b**, complex **3c** showed much lower activity, lower MA incorporation, and lower copolymer molecular weight (Table 2, entry 6 versus entry 3). Complex **3b** was also able to copolymerize ethylene with BVE or AA, at greatly reduced catalytic activity and reduced polar monomer incorporation (Table 2, entries 7−10). However, very high copolymer molecular weight was observed.

The comparison with the classic phosphine-sulfonate palladium complex **PO-Pd** provided interesting results. Similar to the case for ethylene homopolymerization, complex **PO-Pd** was not active in copolymerization at room temperature (Table 2, entry 11). At 100 °C and the same conditions, the catalytic activity of complex **3b** was about half that of complex **PO-Pd** (Table 2, entries 12−14). Two factors might be responsible for the greatly reduced catalytic activity of complex **3b** in copolymerization. First, the cationic palladium center in complex **3b** might be more easily poisoned by MA comonomer than the neutral palladium center in **PO-Pd**. In addition, the BHT inhibitor might also interact with the cationic palladium center in complex **3b**. Both complexes showed similar MA incorporation. However, complex **3b** generated copolymer with molecular weight ca. 3 times higher than that by complex **PO-Pd**. This indicated that the high polymer molecular weight advantage of complex **3b** was maintained in copolymerization. Similar to the case for complex **PO-Pd**, complex **3b** generated E-MA copolymer with the MA unit located predominantly in the main chain on the basis of ^{1}H NMR analysis (Figures S35 and S36 in the Supporting Information).

■ CONCLUSIONS

To conclude, a series of phosphine phosphonic amide ligands and the corresponding palladium complexes were synthesized and characterized. The most distinguishing feature of this ligand framework is that substituents on three positions could be modulated independently, providing a great deal of flexibilities and opportunities to tune the catalytic properties. In comparison with classic phosphine-sulfonate ligands, the electronic and steric properties of the weak σ-donor moiety could also be modified in this ligand structure.

In ethylene polymerization, the phosphine phosphonic amide palladium complex **3b** showed up to 1 order of magnitude higher activity, 6 times higher polyethylene molecular weight, and similar branching density in comparison with the structurally similar classic phosphine-sulfonate palladium complex **PO-Pd**. The activity of complex **3b** could reach up to 1.34×10^7 g mol^{-1} h^{-1}, making it one of the most active palladium catalysts in ethylene polymerization. In ethylene/polar monomer copolymerization, complex **3b** showed lower catalytic activity due to the cationic nature of the palladium center. Similar polar monomer incorporation and ca. 3 times higher copolymer molecular weight were observed for complex **3b** in comparison with **PO-Pd**. Most interestingly, complex **3b** was active for ethylene polymerization and copolymerization with polar monomers at room temperature, while complex **PO-Pd** showed no activity at low temperatures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b01490.

Experimental procedures, NMR spectra for ligands, palladium complexes, polyethylene, and copolymers, and crystal structure data and details of refinement for complexes **2a,e** (PDF)
Crystallographic data for complex **2a** (CIF)
Crystallographic data for complex **2e** (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (NSFC, 21374108, 51522306), Anhui

Provincial Natural Science Foundation (1408085QB28), the Fundamental Research Funds for the Central Universities (WK3450000001), and the Recruitment Program of Global Experts. We thank Dr. S. M. Zhou (HFNL, USTC) for the determination of the crystal structures.

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