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Synthesis of Functional Polyolefins Using Cationic Bisphosphine Monoxide–Palladium Complexes

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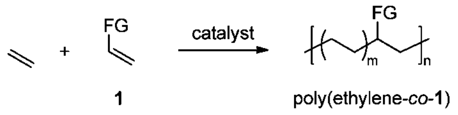
Supporting Information

ABSTRACT: The copolymerization of ethylene with polar vinyl monomers, such as vinyl acetate, acrylonitrile, vinyl ethers, and allyl monomers, was accomplished using cationic palladium complexes ligated by a bisphosphine monoxide (BPMO). The copolymers formed by these catalysts have highly linear microstructures and a random distribution of polar functional groups throughout the polymer chain. Our data demonstrate that cationic palladium complexes can exhibit good activity for polymerizations of polar monomers, in contrast to cationic α-diimine palladium complexes (Brookhart-type) that are not applicable to industrially relevant polar monomers beyond acrylates. Additionally, the studies reported here point out that phosphine-sulfonate ligated palladium complexes are no longer the singular family of catalysts that can promote the reaction of ethylene with many polar vinyl monomers to form linear functional polyolefins.

Despite their ubiquity, polyolefins such as polyethylene and polypropylene are not appropriate for all applications. Polyolefins are inherently nonpolar, which engenders certain material properties such as limited adhesion, dye retention, printability, and compatibility that can restrict their efficacy. Incorporation of polar functional groups into polyolefins even in small amounts, however, can significantly enhance such properties in the resulting 'functional polyolefins'.[1] Thus, the development of methods for the controlled synthesis of functional polyolefins from industrially relevant monomers holds the potential to expand the range of applications available to this indispensible class of materials.

Transition-metal-catalyzed coordination–insertion polymerization of olefins and polar vinyl monomers has recently emerged as a powerful method for the synthesis of functional polyolefins with defined polymer architectures, molecular weight distributions, and comonomer incorporation (Scheme 1).[2,3] The most successful late transition metal complexes that catalyze coordination–insertion polymerization of olefins with polar vinyl monomers have to date been those ligated by α-diimines,[4] or by phosphine-sulfonates.[5] While Pd and Ni complexes ligated by α-diimines catalyze the formation of highly branched polymers,[4b] linear polymer microstructures are obtained with phosphine-sulfonate-ligated Pd and Ni catalysts.[6] Of these two important classes of catalysts, those ligated by phosphine-sulfonates exhibit much higher activity for copolymerizations with challenging polar vinyl monomers such as vinyl acetate,[7] acrylonitrile,[8] vinyl halides,[9] and vinyl ethers[10] compared to catalysts ligated by α-diimines.

Scheme 1



1a: FG = OAc
1b: FG = CH_2OAc
1c: FG = Cl
1d: FG = CH_2Cl
1e: FG = CN
1f: FG = OBu
1g: FG = CO_2Me

An important structural feature of catalysts containing phosphine-sulfonates is the presence of one strong and one weak σ-donor ligand. We hypothesized that palladium complexes containing a bidentate ligand featuring a non-symmetric strong/weak σ-donor framework other than the combination of a phosphine and sulfonate anion could also promote the formation of highly linear, random copolymers by coordination–insertion polymerization, even though such activity across a range of polar vinyl monomers has to date been restricted exclusively within the phosphine-sulfonate family of catalysts.[11] In this study we describe the synthesis of a series of cationic palladium complexes ligated by bisphosphine monoxides (BPMOs) and the successful application of these complexes as catalysts for the polymerization of ethylene and a number of challenging polar vinyl monomers.[12] Our data highlight a new class of transition metal catalyst that effects the formation of highly linear, random copolymers from ethylene and polar vinyl monomers by coordination–insertion polymerization.

The synthesis of BPMO complexes used in this study are summarized in Scheme 2. An admixture of free BPMO and (cod)PdMeCl (cod = 1,5-cyclooctadiene) formed an intermediate (BPMO)PdMeCl complex, which upon treatment with silver(I) salt and 2,6-lutidine afforded complexes **2**–**5** in good isolated yields (49–72%) as air- and moisture-stable solids. We found that homopolymerization of ethylene (3 MPa) occurred in the presence of **2**–**5** (6.0 μmol) in toluene (15 mL) at 80 °C (Table 1). Polymerization activity increased when the substituents on the phosphine were isopropyl rather than phenyl groups. Additionally, the molecular weight of the obtained polyethylene was higher when the substituents on the phosphine oxide moiety of the BPMO ligand were *tert*-butyl rather than phenyl groups. Among complexes **2**–**5**, the highest

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Scheme 2

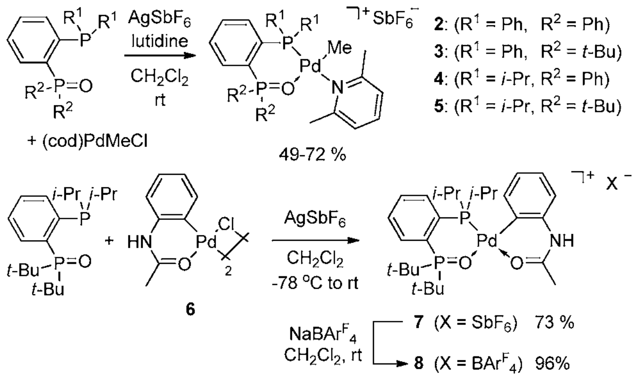

Table 1. Homopolymerization of Ethylene in the Presence of Cationic BPMO−Palladium Complexes[a]

entry	catalyst (μmol)	time (h)	yield (g)	activity (kg mol^{-1} h^{-1})	M_n[b] (10^3)	M_w/M_n
1	**2** (6.0)	3	1.14	63	0.8 (1.8)	1.8
2	**3** (6.0)	3	0.66	36	16 (38)	2.5
3	**4** (6.0)	1	0.79	130	0.9 (1.9)	1.8
4	**5** (6.0)	1	2.01	340	39 (91)	2.3
5[c]	**7** (6.0)	1	1.05	180	12 (27)	3.6
6	**8** (6.0)	1	2.10	350	39 (92)	2.6
7[d]	**5** (0.75)	1	1.41	1900	15 (34)	2.6
8[d]	**7** (0.75)	1	0.94	1300	25 (58)	1.9
9[d]	**8** (0.75)	1	2.11	2800	29 (69)	2.1

[a] Conditions: toluene (15 mL), ethylene (3 MPa), and palladium catalyst (6.0−0.75 μmol) were stirred in a 50 mL stainless steel autoclave at 80 °C. [b] Number-average molecular weight was measured by size-exclusion chromatography using polystyrene as an internal standard and corrected by universal calibration. Molecular weights before universal calibration are shown in parentheses. [c] A mixture of 1 mL of CH_2Cl_2 and 14 mL of toluene was used. [d] 100 °C.

activity (entry 4) was observed when the BPMO substituents were isopropyl groups on the phosphine and *tert*-butyl groups on the phosphine oxide. The polyethylene formed by these cationic BPMO complexes was confirmed by quantitative ^{13}C NMR spectroscopic analysis to be highly linear. For example, only ca. 3 methyl branches per 1000 carbon atoms were observed in the polyethylene formed by catalyst **5** (entry 7), and no higher alkyl branching was detected.

We also prepared stable, coordinatively saturated BPMO−palladacycle precatalysts that obfuscate the additional ancillary ligand (e.g., pyridines) often employed for the synthesis of stable, single-site polymerization precatalysts. The removal of superfluous ancillary ligands proved beneficial for copolymerizations using BPMO−Pd catalysts (vide infra).[13,14] Thus, two new air- and moisture-stable BPMO complexes **7** and **8** were isolated in 73% and 96% yield, respectively, by addition of BPMO to the μ-chloride palladium dimer **6**[15] and subsequent abstraction of chloride by a Ag(I) salt (Scheme 2, bottom).[16] **7** exhibited lower activity (entries 5 and 8) than **5** because of low solubility in toluene. This limitation could be overcome by changing the counteranion from SbF_6 to the weakly coordinating tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BAr^F_4) anion (entries 6 and 9). Using **8**, an *o*-acetanilido palladium BPMO complex having BAr^F_4 as the counteranion, linear polyethylene was formed with an activity of 2800 kg mol^{-1} h^{-1}, which represents one of the more active Pd catalysts for ethylene polymerization reported to date.[17]

The BPMO−Pd complexes **5** and **8** were also successfully applied to the copolymerization of ethylene and polar vinyl monomers (Table 2). Coordination−insertion polymerizations involving vinyl acetate (**1a**) are rare;[7a,18] yet the reaction of ethylene and vinyl acetate proceeded in the presence of either cationic BPMO complex **5** or **8** (entries 1 and 2). Quantitative ^{13}C NMR spectroscopic analysis of the resulting polymers was consistent with vinyl acetate incorporation into the main chain as well as at the initiating and terminating chain ends, based on comparison to previously reported spectroscopic data for

Table 2. Copolymerization of Ethylene and Polar Vinyl Monomers in the Presence of Cationic BPMO−Palladium Complexes[a,b]

entry	catalyst (μmol)	monomer	monomer (mL)	solvent (mL)	temp (°C)	time (h)	yield (g)	activity (kg mol^{-1} h^{-1})	M_n[c] (10^3)	M_w/M_n	incorp.[d] (%)	Me br.[d] (/10^3 C)
1	**5** (20)	**1a** (FG = OAc)	12	3	80	15	0.21	0.72	1.5 (3.4)	2.5	1.3	1.5
2	**8** (10)	**1a**	12	3	80	16	0.18	1.1	1.3 (3.0)	2.5	1.4	1.7
3	**5** (10)	**1b** (FG = CH_2OAc)	3	12	80	12	0.18	1.4	7.5 (17)	2.7	1.0	1.0
4	**8** (10)	**1b**	3	12	80	12	0.94	7.6	15 (35)	2.2	1.2	0.7
5	**5** (20)	**1c** (FG = Cl)	2.4	5	80	89	0.09	0.05	2.7 (6.0)	4.2	0[e]	–
6	**5** (20)	**1d** (FG = CH_2Cl)	3	12	80	20	0.12	0.31	5.8 (13)	1.9	1.1	1.0
7	**8** (10)	**1d**	3	12	80	20	0.18	0.93	8.6 (20)	2.9	0.7	0.6
8	**5** (10)	**1e** (FG = CN)	2.5	2.5	100	86	0.50	0.58	1.4 (3.5)	2.4	2.1	1.8
9	**8** (6)	**1e**	2.5	2.5	100	72	0.30	0.69	1.6 (3.5)	2.7	2.5	0.1
10	**5** (20)	**1f** (FG = OBu)	5	10	80	21	0.28	0.66	9.3 (21)	1.9	2.0	1.4
11	**8** (10)	**1f**	5	10	80	20	0.23	1.2	8.0 (19)	2.4	4.1	0.5
12	**5** (10)	**1g** (FG = CO_2Me)	2.5	2.5	80	18	0	–	–	–	–	–
13	**8** (6)	**1g**	2.5	2.5	80	12	0	–	–	–	–	–

[a] Conditions: catalyst (6−20 μmol), toluene, ethylene (3 MPa), and comonomer were stirred in a 50 mL stainless steel autoclave at the indicated temperature. [b] See Supporting Information for ratios of main chain versus chain end incorporation and turnover numbers for each monomer. [c] Number-average molecular weight was measured by size-exclusion chromatography using polystyrene as an internal standard and corrected by universal calibration. Molecular weights before universal calibration are shown in parentheses. [d] Determined by quantitative ^{13}C NMR analysis. [e] Determined by ^1H NMR analysis ($CDCl_2CDCl_2$, 120 °C).

ethylene/vinyl acetate copolymers.[7a] The activity of **8** compared to **5** was higher, and this activity is higher than the best case reported using catalysts ligated by phosphine-sulfonates, while incorporation ratios of vinyl acetate were similar.

Copolymerization of the related monomer allyl acetate (**1b**) with ethylene was also successful using either BPMO complex **5** or **8** as the catalyst (entries 3 and 4). Similar to the relative activity observed for ethylene/vinyl acetate copolymerization, **8** proved to be more active than **5** for ethylene/allyl acetate copolymerization. The polymer molecular weight (M_n) obtained from the reaction using **8** as the catalyst (entry 4) was higher by a factor of ca. 2 compared to that obtained using a phosphine-sulfonate-ligated catalyst under otherwise identical reaction conditions.[19]

We next explored reactions of halogenated monomers, which are some of the most challenging substrates for coordination–insertion polymerizations due to catalyst poisoning by rapid β-halogen elimination following migratory insertion. Coordination–insertion polymerization of ethylene and vinyl chloride (**1c**), an important halogenated monomer in industry, has not yet been achieved.[9a] While we did isolate a polymer product from the reaction of ethylene and vinyl chloride in the presence of **5** (entry 5), the absence of a resonance corresponding to a chloro methine moiety (–C*H*Cl–) in the ^{1}H NMR spectrum of the product indicates negligible incorporation of **1c**. The low activity and low polymer molecular weight are consistent with previous reports of rapid chain termination and simultaneous catalyst deactivation by β-halogen elimination following insertion of **1c**.[9b,c,20] In contrast, copolymerization of allyl chloride (**1d**) and ethylene in the presence of **5** or **8** was successful (entries 6 and 7). Incorporation of halogenated **1d** into the main chain was confirmed by ^{13}C NMR spectroscopy. The incorporation ratios were similar to that reported for phosphine-sulfonate-based catalysts, but polymer molecular weight (M_n) was again improved by a factor of ca. 2 under otherwise identical reaction conditions.[19]

The polymerization of ethylene and acrylonitrile (**1e**) was accomplished using our cationic BPMO–Pd catalysts (entries 8 and 9). Recent experimental and theoretical studies suggest catalyst inhibition during coordination–insertion polymerization of ethylene and acrylonitrile can be attributed to strong σ-coordination (*N*-bound) over π-coordination of the polar monomer to the metal center, which is an insurmountable obstacle to subsequent migratory insertion for cationic (and electrophilic) α-diimine catalysts that cannot readily participate in π-backbonding.[8c,21] Such logic was used to distinguish why ethylene/acrylonitrile copolymerizations promoted by neutral phosphine-sulfonate-ligated Pd complexes were successful, whereas cationic α-diimine Pd complexes are inactive for this transformation.[8d] Nevertheless, the reaction of ethylene and acrylonitrile in the presence of the cationic complex **5** or **8** indeed provided a polymer product. Analysis of the resulting polymer microstructure by ^{13}C NMR spectroscopy confirmed that acrylonitrile had been incorporated into the polymer main chain, as well as at the initiating and terminating chain ends with incorporation ratios of 2.0–2.5%. While the terminal chain ends in ethylene/acrylonitrile copolymers formed by phosphine-sulfonate-based catalysts were exclusively alkenyl nitrile moieties,[8a] we observed a combination of olefinic chain ends in addition to alkenyl nitrile chain ends for copolymers formed by **5** or **8**. Thus, not only are the activities of cationic BPMO–Pd complexes markedly different from cationic α-diimine Pd complexes for polymerization of ethylene and acrylonitrile, but the microstructure of polymers formed by BPMO-ligated catalysts is also different from those formed by phosphine-sulfonate-ligated catalysts.

The copolymerization of ethylene and vinyl ethers has thus far been difficult with cationic α-diimine Pd catalysts unless the *O*-substituent of the vinyl ether is a bulky silyl group.[10a,b] Concomitant hompolymerization of the vinyl ether in the presence of electrophilic, cationic α-diimine Pd catalysts is particularly problematic. In contrast, we found that cationic BPMO complex **5** or **8** did in fact promote the copolymerization of ethylene and butyl vinyl ether (**1f**) with incorporation ratios of 2.0–4.1% (entries 10 and 11). Analysis of the polymer microstructure by ^{13}C NMR spectroscopy indicates that in-chain incorporation of butyl vinyl ether occurred along with incorporation at the initiating chain end. This result represents only the second example of the copolymerization of simple alkyl vinyl ethers and ethylene by a coordination–insertion pathway.[10c]

Finally, the reaction of ethylene and methyl acrylate (**1g**) was examined using cationic BPMO complexes as catalysts. In the presence of either complex **5** or **8**, no polymer product was isolated after 12–18 h (entries 12 and 13). Although many late transition metal complexes catalyze the copolymerization of ethylene and methyl acrylate,[2] very few can also catalyze the copolymerization of ethylene and other polar monomers such as vinyl acetate, acrylonitrile, and vinyl ethers. In the case of cationic BPMO–Pd complexes such as **5** or **8**, the reactivity profile is exactly reversed. While the origin of the inability of **5** or **8** to catalyze the copolymerization of ethylene and methyl acrylate is currently unclear, these data again highlight some of the unique characteristics of cationic BPMO polymerization catalysts as compared to α-diimine and phosphine-sulfonate based systems.

In summary, we have identified a new family of Pd complexes ligated by bisphosphine monoxides (BPMOs) that act as catalysts for the polymerization of ethylene and polar vinyl monomers. The polar monomers that are applicable to these conditions include some of the historically most challenging polar vinyl monomers for polymerization by a coordination–insertion mechanism. These catalysts lead to copolymers that are highly linear and have a random distribution of the polar monomer throughout the polymer chain. The studies described in this report also provide several perspectives for future development of catalysts for the copolymerization of ethylene and polar vinyl monomers. First, cationic Pd complexes can in fact function as catalysts for coordination–insertion polymerization of ethylene and industrially relevant polar vinyl monomers other than acrylates, even though many prior studies of cationic α-diimine Pd complexes suggest otherwise.

Our data also demonstrate that combinations of a strong and weak σ-donor motif in a bidentate ligand other than the combination of a tertiary phosphine and a sulfonate anion can lead to Pd catalysts that form highly linear, random copolymers by a coordination–insertion mechanism. Future studies will focus on exploring in detail how the BPMO ligand influences the catalyst activity and resulting polymer properties, as well as the identification of new families of bidentate ligands with a weak/strong σ-donor motif that lead to transition metal catalysts for coordination–insertion polymerization with polar vinyl monomers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, characterization of palladium compounds and polymers, and crystallographic data for **7** and $[o\text{-}({}^{i}\mathrm{Pr}_2\mathrm{P})\mathrm{C}_6\mathrm{H}_4(\mathrm{P(O)}{}^{t}\mathrm{Bu}_2)]\mathrm{Pd(Me)(Cl)}$ (**9**). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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