# Thermally Robust Heterobimetallic Palladium-Alkali Catalysts for Ethylene and Alkyl Acrylate Copolymerization

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*Supporting Information Placeholder*

**ABSTRACT:** We report on the synthesis and characterization of a new family of palladium-alkali olefin polymerization catalysts using site-differentiated dinucleating platforms. Metal binding studies indicate that our palladium phosphine phosphonate polyethylene glycol (PEG) complexes form 1:1 adducts with alkali cations in solution, with relative affinities in the order $Na^+ \sim K^+ > Li^+$. We observed that these palladium-alkali complexes are more active for ethylene homopolymerization and ethylene/alkyl acrylate copolymerization compared to their monopalladium counterparts, although their effect on polymer branching and molecular weight is relatively modest. In some cases, the addition of external sodium salts to conventional palladium complexes (i.e. those that do not have pendant PEG chains) also led to remarkable catalyst enhancements, presumably also due to the formation of palladium-sodium species. The unique features of our heterobimetallic systems are that they display long catalyst lifetimes at 100°C and can even operate at temperatures as high as 140°C. Although we have shown that secondary cations clearly increase the electrophilicity of the metal catalyst, their precise role in these polymerization reactions is still under investigation.

## INTRODUCTION

Greater than 70% of the world's ethylene-based polymers is manufactured using transition metal catalyzed processes.[1] Because the intrinsic properties of polyolefins are determined by how their building blocks are assembled,[2] having a broad assortment of metal catalysts to synthesize polyolefins is required to meet the diverse needs of the global market. To be industrially useful, metal catalysts must also be highly active, tolerant of trace impurities, and compatible at high reactor temperatures (e.g. >80°C).[3,4]

The discovery that cationic late transition metal diimine complexes are capable of copolymerizing ethylene with methyl acrylate[5] inspired many researchers to search for new families of polar group compatible molecular catalysts (Chart 1).[6-13] For example, the development of neutral palladium phosphine sulfonate complexes by Drent et. al.[14] has enabled the copolymerization of ethylene with difficult to incorporate polar monomers such as vinyl acetate,[15] vinyl halide,[16,17] acrylonitrile,[18] and acrylamide.[19] Most recently, the research groups of Nozaki[20,21] and Jordan[22,23] disclosed that cationic palladium compounds ligated by *P,O*–ligands also gave active copolymerization catalysts.[24-26] A major drawback in many of these metal-based systems, however, is that the presence of polar monomers causes a significant decrease in catalytic activity compared to in the presence of just ethylene.[9] Furthermore, the molecular weights of the copolymers also tend to be low ($M_n$<$10^5$). In addition to other economic and environmental considerations (e.g. cost, time, waste, etc.), these shortcomings have thus prevented late transition metal complexes from being viable catalysts for commercial polyolefin synthesis.

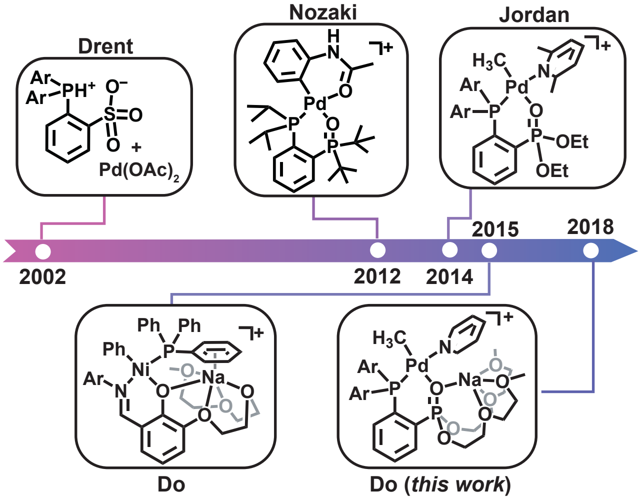


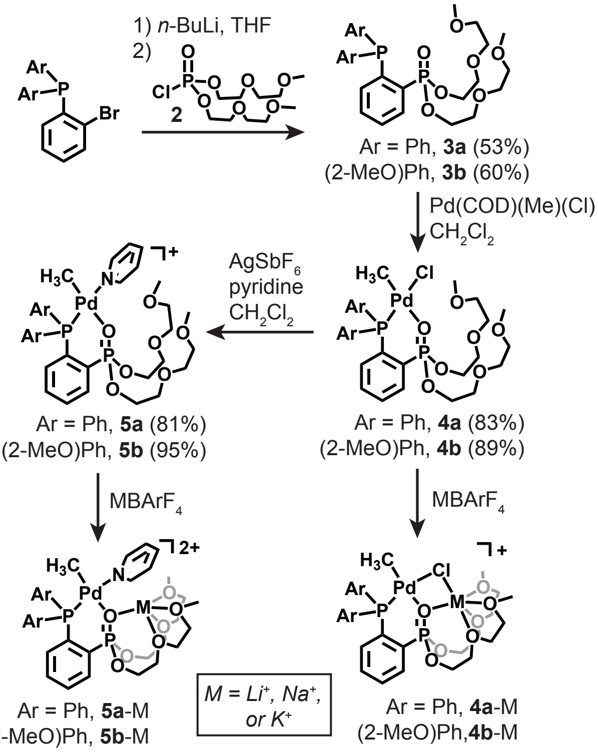
**Chart 1**. Representative examples of late transition metal catalysts for olefin homo- and copolymerization

Our laboratory has been exploring new strategies to overcome the deficiencies of conventional olefin polymerization catalysts. We were inspired by several elegant examples in which Lewis acids were used successfully to promote diverse molecular transformations,[27] including carbon dioxide hydrogenation,[28,29] carbon monoxide insertion,[30,31] dihydrogen activation,[32,33] dioxygen activation,[34,35] and C–H bond oxidation.[36] In previous studies, we discovered that the incorporation of pendant Lewis acids into nickel phenoxyimine[37] polyethylene glycol (PEG) complexes led to dramatic enhancement in their catalyst activity and changes to the microstructures of their polymer products.[38-40] An intriguing question that arose from this work was whether the performance boosting effects of secondary cations is a general catalyst design feature that could be exploited in other molecular polymerization systems.[41] The underlying hypothesis in these studies is that catalysts bearing two functionally distinct metal centers (i.e. heterobimetallics) could work synergistically during polymerization to access reactivity patterns that could not be achieved using either monometallic or homobimetallic catalysts.[42-44] Specifically, secondary Lewis acids could modulate the electrophilicity of the active catalyst or assist in discrete steps during polymerization, such as monomer binding or chain propagation. Although we[38,39] and others[45] have shown that outer sphere interactions with Lewis acidic metal cations could facilitate ethylene homopolymerization, their applications in ethylene and polar vinyl olefin copolymerization have not been explored extensively.[46]

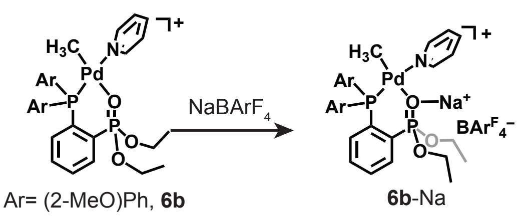
Herein, we demonstrate that the pairing of alkali ions with palladium phosphine phosphonate ester complexes[22] imparts greater reactivity and thermal stability to the parent catalysts in both ethylene homo- and copolymerization. We show that the key to success is the installation of two PEG chains to the ligand's phosphonate group, which provides a well-defined binding site for alkali ions to yield discrete heterobimetallic species even in the presence of excess polar monomers.

## RESULTS AND DISCUSSION

**Synthesis of *P,O*-Ligands and their Palladium Complexes.** Our palladium phosphine phosphonate ester complexes were readily obtained through the synthetic sequence shown in Scheme 1. Lithiation of (2-bromophenyl)diarylphosphine, followed by reaction with methyldiglycol chlorophosphate (**2**), provided ligands **3a** (Ar = phenyl) and **3b** (Ar = 2-methoxyphenyl) in moderate yields. Metallation of these ligands by treatment with Pd(COD)(Me)(Cl) (COD = 1,5-cyclooctadiene) gave complexes **4a** and **4b**, respectively. Chloride abstraction from **4a**/**4b** using $AgSbF_6$ and reaction with pyridine furnished complexes **5a**/**5b**. Single crystals of compounds **4b** and **5b** were analyzed X-ray crystallography (Figures 1A and S60, respectively). In both structures, the palladium center is square planar and the methyl group is *trans* to the phosphonate moiety. The bond metrics at the palladium core in **5b** are similar to those in the analogous diethylphosphonate variant reported by Jordan and coworkers.[22]



**Scheme 1**. Synthesis of ligands **3** and palladium complexes **4** and **5**.



**Scheme 2**. Reaction of complex **6b** with $NaBAr^F_4$ to give **6b**-Na. The $Na^+$ cation is proposed to bind to the P=O donor of **6b** but interactions with the other oxygen atoms of the phosphonate ester are also possible.

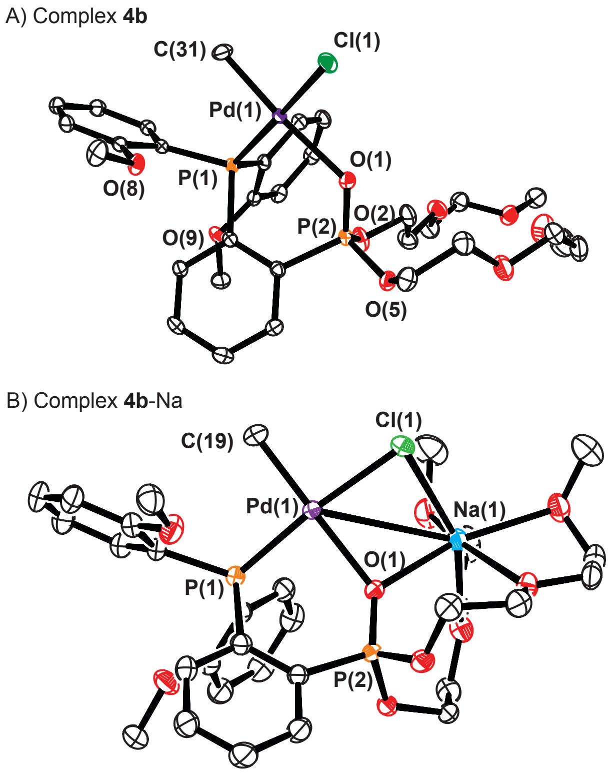


**Figure 1**. X-ray structures of the monopalladium **4b** (A) and heterobimetallic **4b**-Na (B) (ORTEP view, displacement ellipsoids drawn at 50% probability). Hydrogen atoms, and borate anions were omitted for clarity.

**Secondary Alkali Ion Complexation**. To investigate the interactions of our PEGylated palladium compounds with alkali ions, solution studies were carried out in chloroform. Using the method of continuous variation,[47,48] the NMR spectra of **4a** in the presence of various amounts of $MBAr^F_4$ salts ($M = Li^+$, $Na^+$, or $K^+$; $BAr^F_4$ = tetrakis(3,5-trifluoromethylphenyl)borate) were recorded (Tables S1-S3). We observed that the $H_{a1}$ and $H_{a2}$ methylene hydrogen atoms in the PEG chains of **4a** (~4.1 ppm) showed greater chemical shift separations when larger amounts of $M^+$ were present (Figures 2 and S1–S3).[49] This change in $\Delta\delta$ most likely reflects the different local environments of $H_{a1}$ vs. $H_{a2}$ in the more rigid heterobimetallic structures compared to in their monopalladium counterparts. The changes in the chemical shifts of $H_{a1}$ were used to construct Job plots (Figure 3, $X_{Pd}$ is defined as [**4a**]/([**4a**]+[$M^+$]). The peak maxima of the Job plots for **4a**/$M^+$ all occur at $X_{Pd} = 0.5$, which indicates that a 1:1 stoichiometry is optimal between complex **4a** and alkali ions. The slopes of the three plots suggest that the alkali ion affinity of **4a** follows the order $Na^+ \sim K^+ > Li^+$. The dinuclear structure of the palladium-sodium complex **4b**-Na was confirmed by X-ray crystallographic analysis (Figure 1B). The structure revealed that the palladium center in **4b**-Na has the expected square planar geometry, with slightly modified bond distances compared to those in **4b** (Pd–O and Pd–Cl are longer whereas Pd–P and Pd–C are shorter). The sodium ion is six-coordinate due to ligation by five oxygen donors and a bridging chloride. The Pd–Na bond distance is ~3.45 Å.

For complex **5b**, which contains a pyridine donor instead of chloride like in **4b**, similar alkali ion binding behavior was observed (Figures S4-S5). Complexation of $Na^+$ to **5b** led to a downfield shift of the phosphine oxide signal at 22 ppm to 23 ppm in the $^{31}P$ NMR spectrum, which we have attributed to the electron withdrawing effects of sodium. Complex **6b** on the other hand (Scheme 2), showed more minor changes in its NMR spectra when sodium salt was added compared to **5b** (Figures S6–S7). These data suggest that although **6b** can form adducts with $Na^+$, it does so more weakly than **5b**, which is expected since it lacks metal chelating PEG chains. Although our metal binding studies were performed in chloroform rather than in toluene, which is the solvent used in our polymerization studies below, we expect that the optimal 1:1 palladium-alkali binding stoichiometry should still be maintained in the latter.

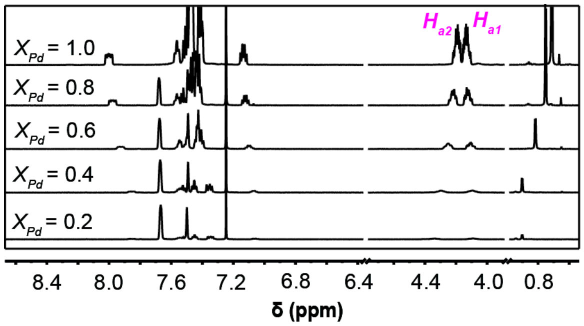


**Figure 2**. $^1H$ NMR spectra ($CDCl_3$, 600 MHz) of complex **4a** and $LiBAr^F_4$ mixed in different ratios. The mole fraction $X_{Pd}$ = [**4a**]/([**4a**]+[$Li^+$]). The peaks labeled as $H_{a1}$ and $H_{a2}$ are assigned to the methylene hydrogen atoms attached to carbon #1 of the PEG chains in **4a**.

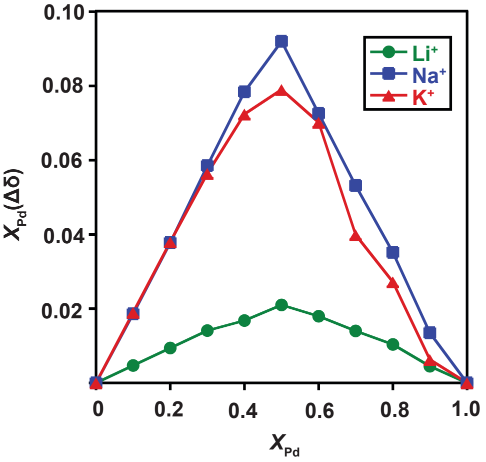


**Figure 3**. Job plots for complex **4a** with $MBAr^F_4$ ($M = Li^+$ (green circles), $Na^+$ (blue squares), $K^+$ (red triangles)) in $CDCl_3$. The total concentration of **4a**/$MBAr^F_4$ is 6 mM for all data points.

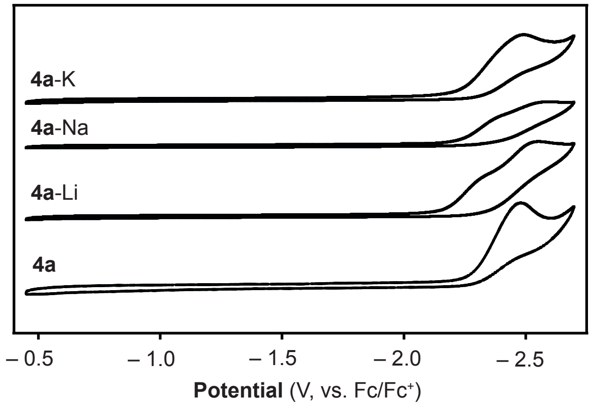


**Figure 4**. Cyclic voltammograms of **4a**, **4a**-Li, **4a**-Na, and **4a**-K complexes (1 mM, bottom to top) recorded in THF at 0.05 V/s in THF with 0.1 M $NBu_4PF_6$ supporting electrolyte. The data were acquired using a glassy carbon working electrode, platinum counter electrode, and silver reference electrode. The reduction potentials measured are as follows: **4a** = -2.5 V, **4a**-Li = -2.2 and -2.5 V, **4a**-Na = –2.3 and -2.5 V, **4a**-K = -2.4 and -2.5 V (difficult to deconvolute due to peak broadness) (vs. $Fc/Fc^+$). The peaks at -2.5 V are assigned to the presence of **4a** rather than from the heterobimetallic palladium-alkali species.

To probe the electronic impact of $M^+$ on the palladium complexes, cyclic voltammetry measurements were conducted (Figure 4). Due to solubility reasons and the highly negative reduction potential of our compounds, THF was used as the electrochemical solvent. In the absence of $M^+$, **4a** displayed a cathodic peak at -2.5 V (vs. ferrocene/ferrocenium), which we have tentatively assigned to reduction of the Pd(II) center. The cyclic voltammograms of **4a**-Li, **4a**-Na, and **4a**-K showed additional broad irreversible waves at approximately -2.2, -2.3, and -2.4 V, respectively,[50,51] and were ascribed to Pd-centered reduction processes in the heterobimetallic species. This trend is consistent with the electrophilicity of the alkali ions,[52] which would be expected to cause a decrease in the electron density at the palladium core through electronic induction.[53] We believe that in THF, an appreciable amount of both monopalladium **4a** and heterobimetallic **4a**-M species are present in equilibrium due to the lower alkali ion binding affinity of **4a** in coordinating solvents compared to in non-coordinating solvents (e.g. chloroform).

**Table 1.** Ethylene Homopolymerization Data for **5a, 5b,** and **6b**.$^a$

| **Entry** | **Complex** | **Salt** | **Polymer Yield** (g) | **Activity** (kg/mol·h) | **Branches**$^b$ (/1000 C) | $M_n{}^c$ ($\times 10^3$) | $M_w/M_n{}^c$ |
|---|---|---|---|---|---|---|---|
| 1 | **5a** | none | trace | 0 | – | – | – |
| 2 | **5a** | $Na^+$ | trace | 0 | – | – | – |
| 3 | **5b** | none | 2.33 | 233 | 7 | 2.17 | 1.27 |
| 4 | **5b** | $Li^+$ | 6.15 | 615 | 11 | 2.15 | 1.65 |
| 5 | **5b** | $Na^+$ | 6.75 | 675 | 10 | 2.90 | 1.46 |
| 6 | **5b** | $K^+$ | 4.67 | 467 | 8 | 2.90 | 1.50 |
| 7 | **6b** | none | 3.95 | 395 | 9 | 1.66 | 1.48 |
| 8 | **6b** | $Na^+$ | 8.95 | 895 | 10 | 1.82 | 1.70 |

$^a$Polymerization conditions: Pd catalyst (5 μmol), $MBAr^F{}_4$ (5 μmol, if any), ethylene (400 psi), 2 mL DCM, 48 mL toluene, 2 h at 80°C. $^b$The total number of branches per 1000 carbons was determined by $^1H$ NMR spectroscopy. $^c$Determined by GPC in trichlorobenzene at 150°C.

**Ethylene Homopolymerization**. Our palladium phosphine phosphonate PEG complexes were tested as catalysts for ethylene homopolymerization (Table 1). We found that at 80°C in toluene under 400 psi of ethylene, complex **5a** was completely inactive (entry 1) whereas complex **5b** displayed moderate activity (entry 3, activity = 233 kg/mol·h). The poor reactivity of **5a** is most likely due to the insufficient steric protection of the palladium center, which is typically required to help promote chain growth over chain termination. In comparison, the Jordan-type catalyst **6b** yielded polyethylene with an activity of 395 kg/mol·h under the same reaction conditions (entry 7).[22] In all cases, the polymers produced were relatively linear (10 branches or less per 1000 carbons) and their molecular weights are low ($M_n$ = ~$1.66–2.17\times10^3$), which is consistent with other reported Pd(*P,O*-ligand) systems.[21] The slower reaction rate of **5b** compared to that of **6b** suggest that the free PEG chains in the former might be self-inhibiting, perhaps by competing with ethylene for coordination to the palladium catalyst.

Next, we proceeded to evaluate the effects of alkali salts on the catalyst's reactivity toward ethylene (Table 1). Using the same polymerization conditions as above, we observed that the reaction of **5b** and $MBAr^F{}_4$ (1:1) with ethylene led to catalytic rate enhancements of about 2.6×, 2.9×, and 2.0× for Li$^+$ (entry 4), Na$^+$ (entry 5), and K$^+$ (entry 6), respectively, compared to **5b** only. The polymer molecular weight and polydispersity remained relatively constant in both the presence and absence of alkali ions. The activity trend observed, Na$^+$>Li$^+$>K$^+$, was somewhat surprising because we noted previously that potassium ions had a more beneficial effect on nickel phenoxyimine-PEG catalysts than lithium ions.[38,39] In the current system, we hypothesize that a *combination* of at least two different factors account for the heterobimetallic effect—the electrophilicity (i.e. Li$^+$>Na$^+$>K$^+$)[52] and the association constant (i.e. Na$^+$~K$^+$>Li$^+$) of the secondary metals.

Interestingly, the reaction of **6b** and NaBAr$^F{}_4$ (1:1) with ethylene led to activity enhancements of about 2.3× compared to **6b** only (Table 1, entry 7 vs. 8). Because **6b** can associate weakly with Na$^+$, presumably via metal chelation by the phosphonate ester group (Figures S6–S7), this result is consistent with our proposed heterobimetallic model. However, we have not discounted other possibilities, such as changes to the solvent medium due to the addition of salts. Since NaBAr$^F{}_4$ does not dissolve in neat toluene without either binding to the palladium catalyst first or mixing with surfactants, it is not likely to contribute to the ionic strength of the reaction solution. To support our claim that the introduction of PEG chains to the ligand platform is beneficial to catalyst stability, we observed that the palladium-sodium **6b**-Na complex is less active at high temperatures compared to PEG-ligated **5b**-Na compounds (vide infra).

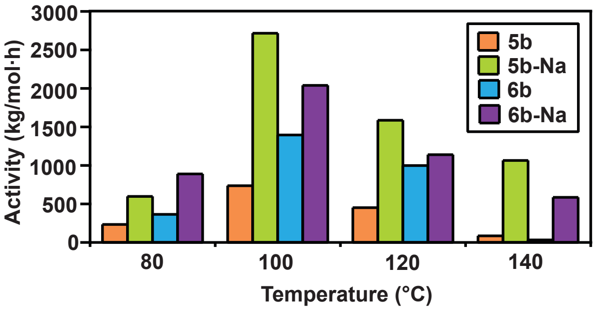


**Figure 5**. Comparison of the activities of catalysts **5b**, **5b**-Na, **6b**, and **6b**-Na in ethylene homopolymerization at various temperatures. See Table S4 for more details.

**Temperature Study**. To determine the optimal reaction temperature, we screened several catalysts in ethylene polymerization from 80 to 140°C in mesitylene/dichloromethane (24:1) for 1 h (Figure 5). For the compounds **5b**, **5b**-Na, **6b**, and **6b**-Na, reactions at 100°C afforded the highest activity and their relative rates were generally observed in the order **5b**-Na > **6b**-Na > **6b** > **5b**. The only exception to this trend is that **6b-Na** is about 1.5× more active than **5b**-Na at 80°C (Table S4, entry 5 vs. 13). At elevated temperatures, however, the opposite was observed. For example, at 140°C, **5b**-Na (1065 kg/mol·h), was about 1.8× faster than **6b**-Na (585 kg/mol·h). In this temperature regime, both palladium-sodium complexes were far more active than their corresponding parent **5b** and **6b** complexes (activity = 85 and 32 kg/mol·h, respectively). Our temperature studies revealed two notable features of this catalyst system. First, for polymerizations conducted at 80°C or below, the addition of stoichiometric amounts of alkali salts to standard palladium phosphine phosphonate ester complexes (e.g. those that are not functionalized with PEG chains) is sufficient to boost catalyst activity. Second, to maximize outer sphere interactions at high temperatures, the catalyst supporting ligands should have suitably strong secondary metal chelators to prevent dissociation of the heterobimetallic structure.

**Time Study**. To examine the catalyst lifetimes, we carried out time-dependent polymerizations for both complexes **5b**-Na and **6b** at 100°C (Table S5). During the period from 15–60 min, both catalysts maintained their catalytic performance. However, **5b**-Na showed about a ~1.9× greater activity (average = 2605 kg/mol·h) than **6b** (average = 1343 kg/mol·h). The thermal robustness of the **5b**-Na complex is exciting from an industrial standpoint because most large-scale commercial solution polymerizations are conducted at 140°C or above.[3] In fact, homogeneous late transition metal catalysts that can operate within this temperature regime are relatively uncommon.[1,54-58]

**Ethylene and Alkyl Acrylate Copolymerization**. Finally, our palladium catalysts were tested in ethylene and methyl acrylate (MA) copolymerization (Table 2). The reaction of **5b** with ethylene/MA at 80°C afforded linear poly(ethylene-co-methyl acrylate) containing ~1.4 mol% of in-chain polar groups (entry 1). Under similar polymerization conditions, the **5b**-M complexes also furnished copolymers with low molecular weight and modest MA ratio. Consistent with our ethylene homopolymerization studies above, the heterobimetallic complexes were more active than their monopalladium counterparts. The highest activity was achieved using 5 equiv. of NaBAr$^F{}_4$ relative to **5b**, which gave about a 2.6× improvement over that of the monopalladium complex itself (compare entry 1 vs. 4). A slight increase in the copolymer $M_n$ was also obtained in the presence of sodium ions ($M_n = 3.15\times10^3$ for **5b**-Na vs. $1.15\times10^3$ for **5b**). The polycrystalline copolymers displayed $T_m$ values ranging from 102-113°C (Table S7). Comparison of the polymerization results between **6b** (entry 6) vs. **6b**-Na (entry 7) showed that the two catalysts behaved quite similarly, although **6b**-Na (64 kg/mol•h) is slightly more active than **6b** (56 kg/mol•h). Interestingly, the main differences between the Jordon-type catalyst **6b** and the heterobimetallic **5b**-M catalysts are that the latter consistently gave copolymers with somewhat higher activity and molecular weight. Although these heterobimetallic effects are relatively small, they do suggest that the addition of alkali salts is beneficial to the copolymerization reactions.

To determine whether methyl acrylate can displace the alkali ions from the heterobimetallic complexes, we measured the $^{1}$H/$^{31}$P NMR spectra of **5b**-Na in the presence of MA (Figures S58-S59). Interestingly, our data showed that the NMR spectra of **5b**-Na remained unchanged when up to 100 equiv. of MA were added. An important point to keep in mind, however, is that under actual catalytic conditions, the amount of MA present is greater than 7000× that of the palladium catalyst. Thus, is it entirely possible that in our polymerization reactions, the dissociation of Na$^{+}$ from **5b**-Na can occur much more readily.

**Table 2**. Ethylene and Alkyl Acrylate Copolymerization Data for **5b** and **6b**.$^{a}$

| **Entry** | **Comonomer** (Conc., M) | **Cat.** | **Salt** (equiv.) | **Temp.** ($^{c}$o.) | **Polymer Yield** (g) | **Activity** (kg/mol•h) | **Branches**$^{b}$ (/1000 C) | ***Inc.***$^{c}$ (%) | $M_n^{d}$ (× 10$^{3}$) | $M_w/M_n^{d}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | MA (1.5) | **5b** | none | 80 | 0.68 | 34 | 7 | 1.4 | 1.15 | 1.67 |
| 2 | MA (1.5) | **5b** | Li$^{+}$(1.0) | 80 | 1.54 | 76 | 5 | 1.5 | 1.63 | 2.00 |
| 3 | MA (1.5) | **5b** | Na$^{+}$(1.0) | 80 | 1.26 | 63 | 5 | 1.5 | 1.73 | 2.17 |
| 4 | MA (1.5) | **5b** | Na$^{+}$(5.0) | 80 | 1.79 | 90 | 5 | 1.4 | 3.15 | 1.24 |
| 5 | MA (1.5) | **5b** | K$^{+}$(1.0) | 80 | 1.22 | 61 | 5 | 1.3 | 1.99 | 2.00 |
| 6 | MA (1.5) | **6b** | none | 80 | 1.12 | 56 | 5 | 1.5 | 0.90 | 2.54 |
| 7 | MA (1.5) | **6b** | Na$^{+}$(1.0) | 80 | 1.28 | 64 | 5 | 1.5 | 0.98 | 1.83 |
| 8$^{e}$ | BA (1.0) | **5b** | none | 100 | 1.41 | 70 | 8 | 1.2 | 1.04 | 1.64 |
| 9$^{e}$ | BA (1.5) | **5b** | none | 100 | 0.86 | 43 | 8 | 1.6 | 1.43 | 1.28 |
| 10$^{e}$ | BA (1.0) | **5b** | none | 120 | trace | 0 | – | – | – | – |
| 11$^{e}$ | BA (1.0) | **5b** | Na$^{+}$(1.0) | 100 | 1.67 | 84 | 6 | 1.2 | 2.30 | 1.47 |
| 12$^{e}$ | BA (1.5) | **5b** | Na$^{+}$(1.0) | 100 | 1.37 | 69 | 6 | 1.9 | 2.48 | 1.56 |
| 13$^{e}$ | BA (1.0) | **5b** | Na$^{+}$(5.0) | 100 | 1.44 | 72 | 6 | 1.7 | 2.14 | 1.41 |
| 14$^{e}$ | BA (1.0) | **5b** | Na$^{+}$(1.0) | 120 | 1.25 | 63 | 7 | 1.3 | 1.73 | 1.55 |
| 15$^{e}$ | BA (1.0) | **6b** | none | 100 | 1.57 | 78 | 5 | 1.0 | 0.99 | 2.16 |
| 16$^{e}$ | BA (1.5) | **6b** | none | 100 | 0.97 | 48 | 8 | 1.7 | 1.03 | 1.93 |
| 17$^{e}$ | BA (1.5) | **6b** | Na$^{+}$(1.0) | 100 | 1.13 | 56 | 8 | 1.6 | 1.14 | 2.07 |

$^{a}$Polymerization conditions: Pd catalyst (10 μmol), MBAr$^{F}_{4}$ (10 μmol, if any), ethylene (400 psi), 50 mL total solution volume in toluene, 2 h. $^{b}$The total number of branches per 1000 carbons was determined by $^{1}$H NMR spectroscopy. $^{c}$Determined by $^{1}$H NMR spectroscopy. $^{d}$Determined by GPC in trichlorobenzene at 150°C. $^{e}$These reactions were performed in mesitylene/dichloromethane (24:1) in a total volume of 50 mL.

To investigate the copolymerization behavior of our catalysts at high temperatures, we replaced MA with *tert*-butyl acrylate (BA) as the polar monomer (Table 2). In general, we observed that increasing the starting BA concentration enhanced the percentage of BA incorporation into the copolymer. Although the addition of sodium salts to **5b** led to modest increases in catalyst activity and molecular weight under certain conditions (e.g. entry 9 vs. 12), its most pronounced effect was on the catalyst's thermal stability. For example, at 120˚C, the activity of **5b**-Na was 63 kg/mol•h (entry 14) whereas that of **5b** was nearly zero (entry 10). For benchmarking, the addition of Na$^{+}$ to **6b** led to a 1.2× improvement in reaction yield (entry 16 vs. 17) at 100˚C. Importantly, all of the poly(ethylene-co-*tert*-butyl acrylate) obtained showed relatively narrow $M_w/M_n$ (1.28–2.23), which suggest that our heterobimetallic catalysts are single-site species.

## CONCLUSION

In summary, we have provided a simple and versatile strategy to site selectively incorporate secondary metals into conventional palladium catalyst platforms. We have shown that the pairing of alkali ions with late transition metal complexes could lead to significant catalyst enhancements, including improvements in their reaction rates and thermal stability. A surprising result in this study was that the addition of external alkali salts to simple palladium phosphine diethylphosphonate complexes was sufficient to generate palladium-alkali species that are more active than their parent complexes. However, we found that the use of PEGylated palladium analogues could better support secondary metals, which was most clearly demonstrated in high temperature polymerization reactions.

This work raises several intriguing questions that still need to be addressed. First, it is unclear what is the precise role of the secondary metals during polymerization. As indicated by cyclic voltammetry measurements, the alkali ions increase the electrophilicity of the palladium complexes. At the same time, however, binding of the alkali metals also leads to bulking up of the catalyst structure. Thus, to what extent does steric vs. electronic factors contribute to the heterobimetallic effect? The precise effects of steric or electronic variations on catalyst reactivity is sometimes difficult to rationalize since other factors such as catalyst stability and solubility could also play a role.[59-61] Second, in our copolymerization studies, the heterobimetallic catalysts seemed to have little influence on the comonomer incorporation ratio compared to the monometallic catalyts. We have preliminary data suggesting that ethylene binding and insertion into palladium-alkyl acrylate intermediates is faster when secondary cations are present. However, how does this change affect the relative rates of other elementary steps in the polymerization process? Future studies will focus on investigating these and other questions, which we anticipate will lead to a better understanding of the use of outer sphere Lewis acids in catalyst design. Ultimately, these studies will allow us to create novel catalyst constructs to access a wider range of ethylene-based polymers for both common and specialized applications.

## EXPERIMENTAL SECTION

**General Procedures**. Commercial reagents were used as received. All air- and water-sensitive manipulations were performed using standard Schlenk techniques or under a nitrogen atmosphere using a glovebox. Anhydrous solvents were obtained from an Innovative Technology solvent drying system saturated with Argon. High-purity polymer grade ethylene was obtained from Matheson TriGas without further purification. The compounds (2-bromophenyl)diphenyl phosphine[62] and Pd(COD)(Me)(Cl)[63] were prepared according to literature procedures.

NMR spectra were acquired using JEOL spectrometers (ECA-400, 500, and 600) and referenced using residual solvent peaks. All $^{13}$C NMR spectra were proton decoupled. $^{31}$P NMR spectra were referenced to phosphoric acid. For polymer characterization: $^{1}$H NMR spectroscopy: each NMR sample contained ~20 mg of polymer in 0.5 mL of 1,1,2,2-tetrachloroethane-*d*$_2$ (TCE-*d*$_2$) and was recorded on a 500 MHz spectrometer using standard acquisition parameters at 120°C.[64] $^{13}$C NMR spectroscopy: Each NMR sample contained ~50 mg of polymer and 50 mM (8.7 mg) chromium acetylacetonate Cr(acac)$_3$ in 0.5 mL of TCE-*d*$_2$ and was recorded at 120°C (125 MHz). The samples were acquired using a 90° pulse of 11.7 μs, a relaxation delay of 4 s, an acquisition time of 0.81 s, and inverse gated decoupling. The samples were preheated for 30 min prior to data acquisition. The carbon spectra were assigned based on the chemical shift values reported in the literature.[12] High-resolution mass spectra were obtained from the mass spectral facility at the University of Houston. Elemental analyses were performed by Atlantic Microlab.

Gel permeation chromatography (GPC) data were obtained using a Malvern high temperature GPC instrument equipped with refractive index, viscometer, and light scattering detectors at 150$^{\circ}$C with 1,2,4-trichlorobenzene (stabilized with 125 ppm BHT) as the mobile phase. A calibration curve was established using polystyrene standards in triple detection mode. All molecular weights reported are based on triple detection.

**Synthesis**. *Preparation of* **4a.** Inside the drybox, compound **3a** (117 mg, 0.21 mmol, 1.0 equiv.) and Pd(COD)(Me)(Cl) (57 mg, 0.21 mmol, 1.0 equiv.) were combined in a small vial and then dissolved in DCM (5 mL) at room temperature. The reaction mixture was stirred at room temperature for 1 h and then filtered through a pipet plug. The filtrate was dried under vacuum. Pentane was added to the residue and stirred until a white solid formed (125 mg, 0.18 mmol, 83%). $^{1}$H NMR (CDCl$_3$, 600 MHz): δ (ppm) = 7.98 (dd, $J_{PH}$ = 5.2 Hz, $J_{HH}$ = 2.0 Hz), 7.55-7.38 (m, 12H), 7.12 (m, 1H), 4.17-4.10 (m, 4H), 3.55-3.44 (m, 12H), 3.31 (s, 6H), 0.69 (d, $J_{PH}$ = 2.4 Hz, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ (ppm) = 136.62 (m), 134.83 (m), 134.45 (d, $J_{PC}$ = 12.7 Hz), 133.16 (m), 132.79 (m), 131.21, 130.76 (d, $J_{PC}$ = 13.2 Hz), 129.63, 129.13, 128.88 (d, $J_{PC}$ = 10.7 Hz), 71.87, 70.35, 69.82 (d, $J_{PC}$ = 6.8 Hz), 66.82 (d, $J_{PC}$ = 5.8 Hz), 59.13, 0.93. (*Note: The signals in the aromatic region could not be assigned due to overlapping peaks*); $^{31}$P NMR (CDCl$_3$, 162 MHz): δ (ppm) = 32.15 (d, $J_{PP}$ = 13 Hz), 20.76 (d, $J_{PP}$ = 13 Hz). Anal. Calc. for $C_{29}H_{39}ClO_7P_2Pd$: C, 49.52; H, 5.59. Found: C,49.34; H, 5.55.

*Preparation of* **4b.** Inside the drybox, compound **3b** (165 mg, 0.27 mmol, 1.0 equiv.) and Pd(COD)(Me)(Cl)

(72 mg, 0.27 mmol, 1.0 equiv.) were combined in a small vial and then dissolved in DCM (5 mL) at room temperature. The reaction mixture was stirred at room temperature for 1 h and then filtered through a pipet plug. The filtrate was dried under vacuum and washed with $Et_2O$ to form a white solid (185 mg, 0.24 mmol, 89%). $^1$H NMR ($CDCl_3$, 600 MHz): δ (ppm) = 7.88 (m, 1H), 7.51-7.46 (m, 3H), 7.41 (t, $J_{HH}$ = 7.2Hz, 1H), 7.34 (br s, 1H), 7.29-7.25 (m, 2H), 6.95 (t, $J_{HH}$ = 7.2 Hz, 2H), 6.91 (dd, $J_{HH}$ = 8.4 Hz, $J_{PH}$ = 4.8 Hz, 2H), 4.22-4.07 (m, 4H), 3.64 (s, 6H), 3.61-3.46 (m, 12H), 3.34 (s, 6H), 0.57 (d, $J_{PH}$ = 3 Hz, 3H). $^{13}$C NMR ($CDCl_3$, 125 MHz): δ (ppm) = 160.72 (d, $J_{PC}$ = 3.8 Hz), 136.52, 136.50 (dd, $J_{PC}$ = 34.9, 10.7 Hz), 134.50 (d, $J_{PC}$ = 15.9 Hz), 134.10 (t, $J_{PC}$ = 6.4 Hz), 133.30, 131.45 (dd, $J_{PC}$ = 6.1, 2.5 Hz), 130.26 (dd, $J_{PC}$ = 185.8, 17.1 Hz), 129.82 (d, $J_{PC}$ = 13.5 Hz), 120.92 (d, $J_{PC}$ = 9.8 Hz), 116.14 (d, $J_{PC}$ = 51.4 Hz), 111.23 (d, $J_{PC}$ = 5.0 Hz), 71.87, 70.35, 70.03 (d, $J_{PC}$ = 7.4 Hz), 66.54 (d, $J_{PC}$ = 6.1 Hz), 59.11, 55.47, -0.22. $^{31}$P NMR ($CDCl_3$, 243 MHz): δ (ppm) = 23.39 (d, $J_{PP}$ = 8.3 Hz), 21.51 (d, $J_{PP}$ = 8.2 Hz). Anal. Calc. for $C_{31}H_{43}ClO_9P_2Pd$: C, 48.77; H, 5.68. Found: C, 48.75; H, 5.85.

*Preparation of* **5a.** Inside the drybox, **4a** (76 mg, 0.11 mmol, 1.0 equiv.) and $AgSbF_6$ (37 mg, 0.11 mmol, 1.0 equiv.) was combined in a small vial. A solution of DCM (5 mL) and pyridine (0.1 mL) was added at room temperature and the reaction mixture was stirred for 1 h. The mixture was then filtered through a pipet plug and the filtrate was dried under vacuum. A solution of $Et_2O$ was added to wash the residue to give a sticky oil (86 mg, 0.09 mmol, 81%). Trace amounts of residual solvent could not be removed completely by vacuum drying. $^1$H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 8.71 (d, $J_{HH}$ = 4.8 Hz, 2H), 8.13 (m, 1H), 7.93 (m, 1H), 7.67-7.47 (m, 14H), 7.15 (m, 1H), 4.07 (m, 4H), 3.54-3.39 (m, 12H), 3.32 (s, 6H), 0.58 (d, $J_{PH}$ = 3.2 Hz, 3H). δ (ppm) = $^{13}$C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 150.11, 139.26, 135.44(m), 134.99 (m), 134.35 (d, $J_{PC}$ = 9.9 Hz), 133.41 (m), 131.97, 131.60, 131.49 (m), 129.39 (d, $J_{PC}$ = 8.8 Hz), 128.29, 127.86, 125.86, 71.76, 70.25, 69.34 (d, $J_{PC}$ = 5.9 Hz), 67.39 (d, $J_{PC}$ = 5.8 Hz), 59.01, 3.95. (*Note: The signals in the aromatic region could not be assigned due to overlapping peaks*); $^{31}$P NMR ($CDCl_3$, 243 MHz): δ (ppm) = 33.11 (d, $J_{PP}$ = 19.4 Hz), 21.01 (d, $J_{PP}$ = 19.4 Hz).

*Preparation of* **5b.** Inside the drybox, **4b** (155 mg, 0.20 mmol, 1.0 equiv.) and $AgSbF_6$ (70 mg, 0.20 mmol, 1.0 equiv.) was combined in a small vial. A solution of DCM (10 mL) and pyridine (0.1 mL) was added at room temperature and the reaction mixture was stirred for 1 h. The mixture was then filtered through a pipet plug and the filtrate was dried under vacuum. A solution of $Et_2O$ was added to wash the residue to give a sticky oil (201 mg, 0.19 mmol, 95%). Trace amounts of residual solvent could not be removed completely by vacuum drying. $^1$H NMR ($CDCl_3$, 600 MHz): δ (ppm) = 8.67 (d, $J_{HH}$ = 3.6 Hz, 2H), 7.97 (m, 1H), 7.92 (t, $J_{HH}$ = 7.2 Hz, 1H), 7.58-7.56 (m, 5H), 7.51 (t, 7.8 Hz, 1H), 7.43-7.31 (m, 3H), 7.05 (t, $J_{HH}$ = 7.8 Hz, 2H), 6.99 (dd, $J_{HH}$ = 8.4 Hz, $J_{HH}$ = 4.8 Hz, 2H), 4.00-3.87 (m, 4H), 3.68 (s, 6H), 3.54-3.42 (m, 12H), 3.32 (s, 6H), 0.39 (d, $J_{PH}$ = 3.6 Hz, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 160.70 (d, $J_{PC}$ = 2.9 Hz), 150.15, 139.02, 136.80 (d, $J_{PC}$ = 11.7 Hz), 135.03 (d, $J_{PC}$ = 16.5 Hz), 134.62 (dd, $J_{PC}$ = 26.2, 3.6 Hz), 134.36, 134.05 (t, $J_{PC}$ = 8.3 Hz), 132.15 (d, $J_{PC}$ = 16 Hz), 130.52 (d, $J_{PC}$ = 14.5 Hz), 128.95 (dd, $J_{PC}$ = 187.6, 17.6 Hz), 125.70, 121.27 (d, $J_{PC}$ = 11.6 Hz), 114.49 (d, $J_{PC}$ = 56 Hz), 111.73, 71.77, 70.28, 69.42 (d, $J_{PC}$ = 5.8 Hz), 66.84 (d, $J_{PC}$ = 6.8 Hz), 59.02, 55.56, 3.19. $^{31}$P NMR ($CDCl_3$, 243 MHz): δ (ppm) = 23.93 (d, $J_{PP}$ = 14.3 Hz), 21.54 (d, $J_{PP}$ = 14.3 Hz).

*Preparation of* **6b**. Inside the drybox, the palladium phosphine diethylphosphonate chloride complex[22] (115 mg, 0.19 mmol, 1.0 equiv.) and $AgSbF_6$ (65 mg, 0.19 mmol, 1.0 equiv.) were combined in a small vial. A solution of DCM (10 mL) and pyridine (0.1 mL) was added at room temperature and the reaction mixture was stirred for 1 h. The mixture was then filtered through a pipet plug and the filtrate was dried under vacuum. A solution of $Et_2O$ was added to wash the residue to give a white solid (149 mg, 0.17 mmol, 89%). $^1$H NMR ($CDCl_3$, 600 MHz): δ (ppm) = 8.66 (d, $J_{HH}$ = 4.9 Hz, 2H), 7.93 (t, 7.8 Hz, 1H), 7.83 (m, 1H), 7.62-7.53 (m, 6H), 7.38-7.34 (m, 3H), 7.05 (t, $J_{HH}$ = 7.5 Hz, 2H), 6.99 (dd, $J_{HH}$ = 8.4 Hz, $J_{HH}$ = 4.8 Hz, 2H), 3.87(m, 4H), 3.68 (s, 6H), 1.10 (t, $J_{HH}$ = 7.0 Hz, 6H), 0.38 (d, $J_{PH}$ = 3.0 Hz, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 160.66 (d, $J_{PC}$ = 2.2 Hz), 150.11, 139.14, 136.81 (d, $J_{PC}$ = 11.3 Hz), 135.24 (d, $J_{PC}$ = 14.1 Hz), 134.80 (dd. $J_{PC}$ = 46.7, 11.4 Hz) 134.36, 133.42 (dd, $J_{PC}$ = 9.3, 8.2 Hz), 132.11 (d, $J_{PC}$ = 7.0 Hz), 130.63 (d, $J_{PC}$ = 12.2 Hz), 129.18 (dd, $J_{PC}$ = 184.7, 17.5 Hz) 125.74, 121.24 (d, $J_{PC}$ = 11.3 Hz), 114.49 (d, $J_{PC}$ = 56 Hz), 111.73 (d, $J_{PC}$ = 4.4 Hz), 64.44 (d, $J_{PC}$ = 6.4 Hz), 55.58, 15.89 (d, $J_{PC}$ = 6.5 Hz), 3.12. $^{31}$P NMR ($CDCl_3$, 243 MHz): δ (ppm) = 24.11 (d, $J_{PP}$ = 14.1 Hz), 21.08 (d, $J_{PP}$ = 14.1 Hz).

**Metal Binding Studies.** The method of continuous variation (Job Plot analysis) was used to determine the binding stoichiometry of our palladium complexes with alkali ions.[48] To perform these experiments, stock solutions of **4a** (6 mM, 6 mL) and $MBAr^F{}_4$ (6 mM, 15 equiv. $Et_2O$ to solubilize the salts, 6 mL, M = $Li^+$, $Na^+$, or $K^+$) were prepared separately in $CDCl_3$. Various amounts of each stock solution were added to an NMR tube so that a total volume of 1 mL was obtained. Ten different NMR samples were prepared, each containing a different ratio of **4a**:M. The samples were recorded at room temperature by $^1$H NMR spectroscopy. As shown in Figures S1-S3, the two hydrogen resonances centered at ~4.1 ppm corresponding to the C1 methylene unit of the PEG chains in **4a** shift in the presence of alkali ions. The chemical shift separation between $H_{a1}$ and $H_{a2}$ increases as the Pd mole fraction decreases. The changes in the $^1$H

NMR signals of $H_a$ as a function of the mole fraction of **4a** are provided in Tables S1-S3.

**Ethylene Polymerization:** Inside the drybox, the palladium complexes (5 μmol) and alkali salts (5 μmol) were dissolved in 10 mL of toluene/DCM (8:2) and stirred for 10 mins. By visual inspection, the resulting palladium-alkali complexes appeared to be soluble in the reaction mixture. The mixture was sealed inside a vial using a rubber septum and brought outside of the drybox. Under an atmosphere of $N_2$, the catalyst solution was loaded into a syringe. To prepare the polymerization reactor, 40 mL of dry toluene was added to an empty autoclave and preheated to the desired temperature. The autoclave was purged with ethylene (20 psi) for 1 min and then the catalyst solution was injected into the autoclave via syringe. The reactor pressure was increased to 400 psi of ethylene and the contents were stirred vigorously for 2 h. To stop the polymerization, the autoclave was vented and cooled in an ice bath. A solution of MeOH (100-200 mL) was added to precipitate the polymer. The polymer was collected by vacuum filtration, rinsed with MeOH, and dried under vacuum at $80^{o}$C overnight. The reported yields are average values of triplicate runs and typically have less than 5% deviation by weight.

**Ethylene and Alkyl Acrylate Copolymerization:** Inside the drybox, the palladium complexes (10 μmol) and alkali salts (10 μmol) were dissolved in 2 mL of DCM and stirred for 10 mins. The mixture was sealed inside a vial using a rubber septum and brought outside of the drybox. Under an atmosphere of $N_2$, the alkyl acrylate comonomer was add into the catalyst solution and the final mixture was loaded into a syringe. To prepare the polymerization reactor, 39-41 mL of dry toluene or mesitylene was added to an empty autoclave and preheated to the desired temperature. The autoclave was purged with ethylene (20 psi) for 1 min and then the catalyst solution was injected into the autoclave via syringe. The reactor pressure was increased to 400 psi of ethylene and the contents were stirred vigorously for 2 h. To stop the polymerization, the autoclave was vented and cooled in an ice bath. A solution of MeOH (100-200 mL) was added to precipitate the polymer. The polymer was collected by vacuum filtration, rinsed with MeOH, and dried under vacuum at $80^{o}$C overnight. The reported yields are average values of triplicate runs and typically have less than 5% deviation by weight

## ASSOCIATED CONTENT

**Supporting Information**.
The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, characterization of compounds and polymers, NMR spectra, and crystallographic data (PDF).

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### Notes

The authors declare no competing financial interests.

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