

Water as an Activator for Palladium(II)-Catalyzed Olefin Polymerization

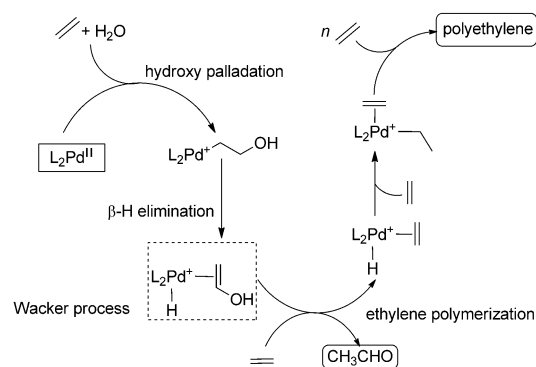
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Abstract: By a reasonable combination of the Wacker reaction and olefin polymerization processes, water proves to be an excellent activator for the palladium(II)-catalyzed polymerization of ethylene and it provides a safe, environmental-friendly and handy initiator for olefin polymerization. The activity of the olefin polymerization is comparable to reactions catalyzed by the corresponding alkylated cationic palladium complexes.

Keywords: olefins · palladium · polymerization · Wacker reaction · water chemistry

Introduction

Since Brookhart's pioneering works in the 1990s,^[1–7] Pd^{II}-diimine complexes have been widely employed as precatalysts for olefin polymerization, producing various polyolefins with attractive structures and properties.^[1–3] For example, in the polymerization of ethylene and copolymerization of ethylene with polar olefins reported by Brookhart,^[1] in the control of polyethylene (PE) topology through chain walking reported by Guan,^[2] and in Mecking's aqueous coordination polymerizations of ethylene based on the water-insolubility of catalyst precursors and the encapsulation effect,^[3] the Pd^{II}-diimine complexes exhibited unique reactivity. However, in all of the aforementioned polymerizations, either presynthesized cationic alkyl-palladium(II)-diimine complexes were employed or methylaluminoxane (MAO) was used as a cocatalyst.^[3a] Feldman and co-workers reported an elegant ethylene polymerization that took place at pressures above 300 psi with [ArN=C(Me)C(Me)=NArPd(MeCN)₂][BF₄]₂ (Ar=2,6-(iPr)₂C₆H₃) without activator, in which they found that activity was reduced by the presence of more than trace amounts of water, but the mechanism was unclear.^[8] Recently, Labinger and Bercaw et al.^[9] documented that, in the presence of the desired amount of water, a [(ArN=C(Me)C(Me)=NAr)Pd(μ-OH)]₂²⁺ (Ar=3,5-(CMe₃)₂C₆H₃/trifluoroethanol (TFE) system can promote the oligomerization of ethylene and propylene, as well as the isomerization/oligomerization of 1-hexene. The aforementioned reports and mechanistic studies on the Brookhart catalyst system have revealed that [LnPd⁺-H] species, formed by β-H elimination of [LnPd⁺-alkyl], is the



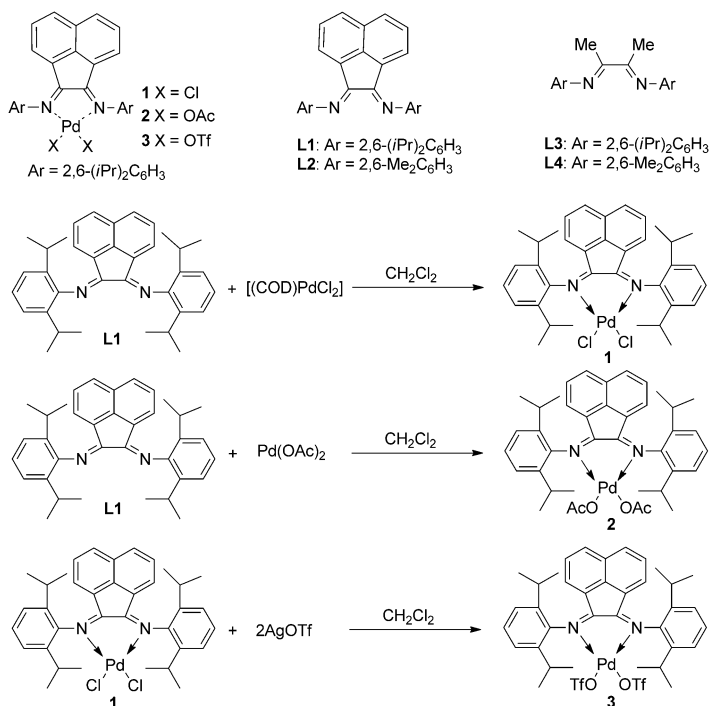
Scheme 1. Strategy for H₂O-initiated polymerization of ethylene.

initial catalytic species.^[14] Combined with the fact that [Pd⁺-H] can be generated by the Wacker reaction^[10] of ethylene and water (Scheme 1, left side), we envisioned that the Wacker process may be integrated into ethylene polymerization to provide [Pd⁺-H] species to initiate olefin polymerization. The challenge^[11] is the control of the conflict associated with β-H elimination in two processes, in which fast β-H elimination is desired in the Wacker reaction to generate [Pd⁺-H] whereas it has to be inhibited in the olefin polymerization. Very recently, we developed a water-initiated facile and efficient palladium(II) ethylene polymerization system in which the Wacker process was successfully integrated into the polymerization system to provide the key palladium-hydride species, without the need to prepare alkylated palladium precursors or organometallic activators. The role of water is clarified. In this paper, we wish to report the results in details.

Results and Discussion

Synthesis of α-diimine-palladium(II) complexes: The procedures for the preparation of palladium(II) complexes **1**, **2**, and **3** are shown in Scheme 2. **L1–L4** were synthesized according to known procedures.^[1h]

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Scheme 2. Synthesis of α -diimine–palladium(II) complexes.

All of the palladium complexes were characterized by NMR and elemental analyses. Fortunately, single crystals of **3**^[12] ($X = \text{OTf}$) that were suitable for X-ray diffraction analysis were formed from CH_2Cl_2 solution. As shown in Figure 1, the crystal structure of **3** displays a square-planar geometry. Similar to the structure of $[\text{ArN}=\text{C}(\text{Me})\text{C}(\text{Me})=\text{NAr}]\text{Pd}(\text{CH}_3)_2$, ($\text{Ar} = 2,6\text{-}(i\text{Pr})_2\text{C}_6\text{H}_3$),^[11] the aryl rings on the aniline moieties are oriented approximately perpendicular to the chelated ring.

Ethylene polymerization: Initially, we used diimine– PdCl_2 **1** to test the water-initiated polymerization of ethylene because PdCl_2 is the most commonly used catalyst for the Wacker reaction. Unfortunately, it failed to promote the polymerization. Considering cationic Pd^{II} should be more efficient for the activation of ethylene and speed up the Wacker reaction to generate palladium–hydride for the polymerization, we synthesized and evaluated Pd^{II} complexes **2** and **3** for comparison. As shown in Table 1, diimine– $\text{Pd}(\text{OAc})_2$ **2** also failed to promote ethylene polymerization. However, when $\text{Pd}(\text{OAc})_2$ was replaced by $\text{Pd}(\text{OTf})_2 \cdot 2\text{H}_2\text{O}$, we are pleased to find that the desired polymerization worked well at 25°C under 1 atm ethylene in the presence of 2.0 equivalents of water (entry 3). Indeed, water proved to be essential to activate the Pd complexes for the polymerization. Although we cannot make the solvent completely free of water (2.5–4.0 ppm), as expected, without additional water, decreased activity was observed (entry 4). Increasing the amount of water revealed a maximum polymerization activity (entries 4–10), and when 50 equivalents of water was added the reactivity increased by nearly an order

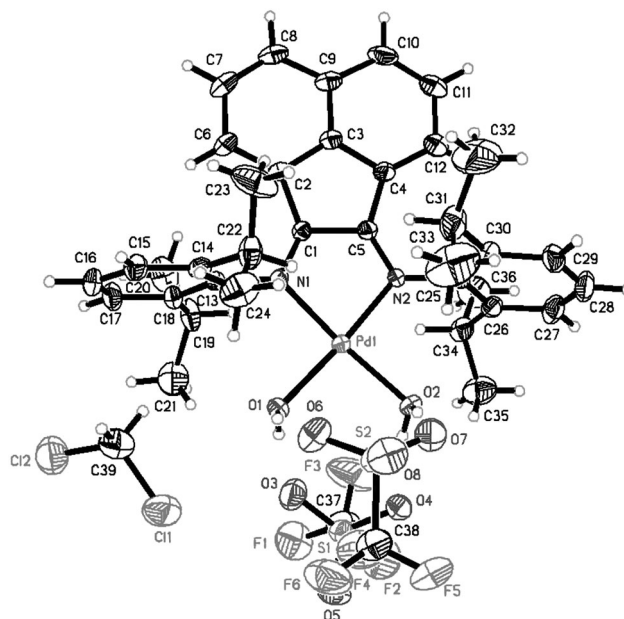


Figure 1. Molecular structure of **3**. Selected bond lengths [Å] and angles [°]: Pd(1)–O(1) 2.040(3), Pd(1)–O(2) 2.039(3), Pd(1)–N(1) 2.001(3), Pd(1)–N(2) 1.993(3), N(1)–C(13) 1.444(4), N(2)–C(25) 1.434(4), N(1)–N(2) 2.625(4); O(1)–Pd(1)–N(1) 93.51(12), O(1)–Pd(1)–O(2) 91.66(12), N(1)–Pd(1)–N(2) 82.18(11), O(2)–Pd(1)–N(2) 92.64(11), C(1)–N(1)–C(13)–C(14) 93.4(4), C(5)–N(2)–C(25)–C(30) 79.3(4).

Table 1. Water-initiated polymerization.^[a]

Entry	Cat.	Water [equiv]	Activity [g per mmol-Pd·h]	$M_{w,\text{GPC}}^{\text{[c,d]}}$	$M_w/M_n^{\text{[c]}}$	$M_{w,\text{LLS}}^{\text{[d,e]}}$
1	1	2.0	– ^[b]	–	–	–
2	2	2.0	– ^[b]	–	–	–
3	3	2.0	1.2	0.84	3.13	1.91
4	3	0	0.8	0.84	1.49	1.85
5	3	5.0	1.1	0.87	2.65	1.94
6	3	10.0	2.0	0.74	3.62	1.63
7	3	50.0	8.7	0.59	1.65	1.22
8	3	100.0	7.4	0.54	1.90	1.05
9	3	200.0	2.5	0.53	2.52	1.17
10	3	500.0	0.6	0.44	3.72	0.93

[a] Reaction conditions: catalyst (50 μmol), CH_2Cl_2 (50 mL), ethylene (1 atm), 6 h, 25°C . [b] No product was observed. [c] Determined by GPC analysis. [d] 104 g mol^{-1} . [e] Determined by LLS analysis.

of magnitude in comparison to the reaction without additional water (entry 4 vs. entry 7). Thus, H_2O successfully initiated ethylene polymerization catalyzed by complex **3**.

The molecular weight of the polyethylene decreased as the amount of water was increased (Table 1, entries 3–10), suggesting that by changing the amount of water the molecular weight of the polymer in our system could be adjusted. The reason behind this phenomenon is probably chain transfer to water.^[15] When a low amount of water is present (entries 3–5), the molecular weight of the polyethylene was similar to that achieved by the cationic alkylated palladium complex.^[2a]

Because it has been documented^[13] that the Wacker reaction with pyridine-coordinated $[\text{PdCl}_3]^-$ is much slower (by

ca. 750-fold) relative to $[\text{PdCl}_4]^{2-}$, we supposed that the polymerization might be hampered by the retarded Wacker reaction initiated by **3**. When one-pot polymerization was tried, to our delight, much higher activity was observed by using mixed ligand **L1** generated in situ with $\text{Pd}(\text{OTf})_2 \cdot 2\text{H}_2\text{O}$ rather than complex **3** (Table 2, entry 1 vs.

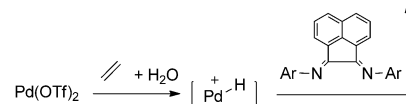
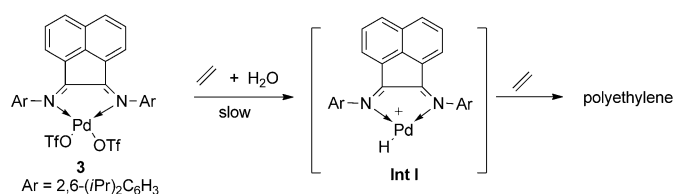
Table 2. Ligand effects on the one-pot ethylene polymerization.^[a]

Entry	Complex	Yield [g]	Act. ^[b]	$M_{w,\text{GPC}}^{\text{[c,d]}}$	$M_w/M_n^{\text{[c]}}$	$M_{w,\text{LLS}}^{\text{[d,e]}}$
1 ^[f]	3	0.32	1.07	0.82	1.41	9.19
2	L1 /[Pd]	1.69	5.63	0.72	1.41	7.50
3	L2 /[Pd]	0.90	2.98	0.25	2.20	2.46
4	L3 /[Pd]	6.34	21.13	0.46	1.25	4.23
5	L4 /[Pd]	2.25	7.50	0.68	1.46	6.95

[a] Reaction conditions: ligand (75 μmol), $\text{Pd}(\text{OTf})_2 \cdot 2\text{H}_2\text{O}$ (50 μmol), DCE (50 mL), ethylene (1 atm), 6 h. [b] g per mmol-Pd-h. [c] Determined by GPC analysis. [d] 10^4 g mol^{-1} . [e] Determined by LLS analysis. [f] Complex **3**: 50 μmol .

2). This may be ascribed to the fact that the coordination of the diimine ligand to $\text{Pd}(\text{OTf})_2$ decreases the Lewis acidity of the palladium and slows down the hydroxyl-palladation step (Scheme 1), which is the rate-determining step in the Wacker reaction.^[13] In the one-pot system, part of the $\text{Pd}(\text{OTf})_2 \cdot 2\text{H}_2\text{O}$ was supposed to promote the Wacker reaction to generate palladium-hydride, followed by coordination of the diimine ligand (Scheme 3).^[14] As a result, both the efficiency of the generation of the active species **INTI** and the polymerization activity are increased. Using this protocol, several diimine ligands (**L1–L4**) were examined and **L3**/ $\text{Pd}(\text{OTf})_2 \cdot 2\text{H}_2\text{O}$ was found to give the highest activity (21.13 g per mmol-Pd-h) under 1 atm ethylene pressure at 25 °C (Table 2, entry 4), which was comparable to that obtained with the corresponding alkylated Pd^{II} catalyst.^[14]

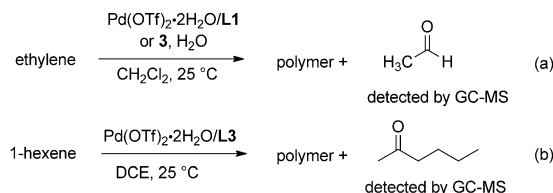
The influences of solvent, catalyst concentration, and temperature were examined. As shown in Table 3, 1,2-dichloroethane (DCE) was found to be more suitable than PhCl and toluene (entries 2, 10, and 11). The activity was nearly doubled when $\text{Pd}(\text{OTf})_2$ concentration was increased from 0.5 to 1.0 mM (entries 1 and 2), whereas further increasing its concentration to 2.0 mM did not enhance the activity further (entry 3). Under the optimized conditions, the best result was achieved when polymerization was performed at 25 °C (entry 2). The catalyst system is quite stable and ethylene polymerization continued for at least 6 h (entries 2, and 6–8). Higher ethylene pressure could further increase the yield of polymer formation (entry 7 vs. 9). Under the same conditions, 1-hexene also polymerized to give polyhexene (entry 12). All polymers generated were colorless oils. ^1H and ^{13}C NMR spectroscopic studies showed that the polymers were highly branched,^[15] similar to those obtained with the corresponding cationic palladium methyl complexes.^[16] The ratios of $M_{w,\text{LLS}}$ to $M_{w,\text{GPC}}$ also indicated the highly branched struc-



Scheme 3. New strategy for the generation of $[\text{LnPd}^+-\text{H}]$.

ture of the polymers, which are very useful as lubricants and plastic additives.^[16]

Mechanistic study: As was initially proposed in Scheme 1, acetaldehyde should be formed as a byproduct during the polymerization reaction. After carefully adjusting the parameters, GC-MS was employed as a convenient method to monitor acetaldehyde formation. As shown in Scheme 4,



Scheme 4. Detection of acetaldehyde and 2-hexanone.

acetaldehyde was detected in the cases of both **L1**/ $\text{Pd}(\text{OTf})_2 \cdot 2\text{H}_2\text{O}$ and **3**/ H_2O (Scheme 4a). Under similar conditions, 1-hexene also underwent polymerization and, as expected, 2-hexanone was also detected by GC-MS analysis (Scheme 4b).^[17]

Table 3. Olefin polymerization of $\text{Pd}(\text{II})$ initiated by water.^[a]

Entry	$\text{Pd}(\text{OTf})_2 \cdot 2\text{H}_2\text{O}$ [μmol]	t [h]	T [°C]	Yield [g]	Act. ^[b]	$M_{w,\text{GPC}}^{\text{[c,d]}}$	$M_w/M_n^{\text{[c]}}$	$M_{w,\text{LLS}}^{\text{[d,e]}}$
1	25	6	25	1.85	12.33	0.52	1.16	5.28
2	50	6	25	6.34	21.13	0.46	1.25	4.23
3	100	6	25	10.0	16.67	0.42	1.27	5.20
4	50	6	0	1.27	4.23	2.29	3.12	8.44
5	50	6	40	2.86	9.53	0.55	1.23	5.53
6	50	1	25	2.80	56.0	0.51	1.24	6.04
7	50	2	25	3.80	38.0	0.49	1.23	5.27
8	50	4	25	5.13	25.7	0.47	1.21	4.86
9 ^[f]	50	2	25	9.64	96.39	0.43	1.33	3.70
10 ^[g]	50	6	25	2.30	7.67	0.04	3.32	–
11 ^[h]	50	6	25	1.38	4.60	0.01	2.51	–
12 ^[i]	50	6	25	0.11	0.40	0.40	3.06	0.47

[a] Reaction conditions: **L3** (1.5 equiv), $\text{Pd}(\text{OTf})_2 \cdot 2\text{H}_2\text{O}$ (1.0 equiv), DCE (50 mL), ethylene (1 atm), 6 h. [b] g per mmol-Pd-h. [c] Determined by GPC analysis. [d] 10^4 g mol^{-1} . [e] Determined by LLS analysis. [f] ethylene (8 atm). [g] Solvent: PhCl (50 mL). [h] Solvent: toluene (50 mL). [i] 1-Hexene (10.0 mL), **L1** (75 μmol), no ethylene.

To investigate further the Wacker process involved in the polymerization initiation, we determined the GC yield of acetaldehyde produced during the one-pot polymerization. Heptane was chosen as an internal standard, and the average correction factor between acetaldehyde and heptane was determined to be 2.80.^[15b] Under the standard ethylene polymerization conditions, consistently more than 80% GC yield of acetaldehyde (based on Pd) was detected,^[18] suggesting that the Wacker process is truly involved in the polymerization.

To further confirm the proposed mechanism, we attempted to correlate the amount of polyethylene and acetaldehyde produced during the one-pot polymerization. As shown in Figure 2, the amount of the polyethylene is nicely

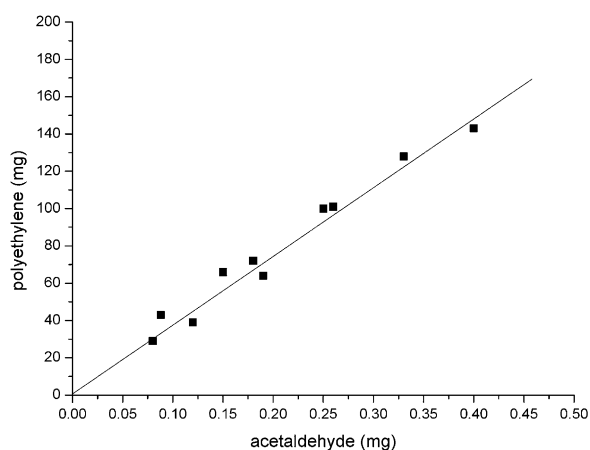


Figure 2. Relationship between acetaldehyde and polyethylene. The polymerizations were performed with **L1**/Pd(OTf)₂·2H₂O.

Table 4. Relationship between acetaldehyde and polyethylene.^[a]

Entry	Pd(OTf) ₂ ·2H ₂ O [mg]	Heptane [mg]	CH ₃ CHO [mg]	Polymer [mg]
1	8.4	5.3	0.40	143
2	7.1	7.5	0.33	128
3	6.0	9.9	0.26	101
4	5.8	4.1	0.25	100
5	4.4	8.0	0.18	72
6	3.6	5.1	0.15	66
7	3.6	8.3	0.19	64
8	2.7	5.6	0.088	43
9	2.8	7.5	0.12	39
10	1.4	5.5	0.08	29

[a] Pd(OTf)₂·2H₂O (1.0 equiv), **L1** (1.5 equiv, 18.5 μmol mL⁻¹), CH₂Cl₂ (10 mL), H₂O(μL)/Pd(mg)=1, 0.5 h, 25 °C.

proportional to the amount of acetaldehyde when different amounts of **L1**/Pd(OTf)₂·2H₂O was used (Table 4). Moreover, by varying the amount of water at a fixed Pd^{II} concentration, the amount of polyethylene was also found to be directly proportional to the amount of acetaldehyde.^[15b] Because acetaldehyde can only be produced by the Wacker process, the nearly linear correlation between the amount of polyethylene and acetaldehyde supports well the fact that water is essential in the activation of the precatalysts and

that polymerization activity depends on the Wacker process. This result further proved that the polymerization is initiated, at least mainly, by the Wacker reaction, and differs from Bercaw's system, in which oligomerization of the olefin became very slow (on the order of days) in the absence of TFE and when Ar is 2,6-(CHMe₂)₂C₆H₃, the dimer complex is completely inert.

Conclusion

In the transition-metal-catalyzed coordination polymerization of olefins, the activator plays an important role.^[19] Although a variety of activators have been developed for different precatalysts^[1-7] in the past decades, most involve metal alkyl compounds such as triethylaluminum and MAO, which are usually air- and moisture-sensitive.^[19] In the current work, water was identified as an excellent activator for the cationic palladium(II)-catalyzed ethylene polymerization, providing a safe, environment-friendly and handy initiator for olefin polymerization. Under the optimal conditions, the activity of the polymerization is comparable to that catalyzed by alkylated cationic palladium complexes. The presynthesis of alkylpalladium complexes or the use of metal alkyl compounds such as triethylaluminum and MAO, is not necessary, making the palladium(II)-catalyzed olefin polymerization very simple. The success of the integration of the Wacker reaction into the olefin polymerization process should pave the way for the development of new activators for Pd^{II}-catalyzed olefin polymerization.

Experimental Section

General remarks: All air- or moisture-sensitive manipulations were carried out under a nitrogen atmosphere either by using Schlenk techniques or in a glove box. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury 300 or Varian 400 MR spectrometer. Mass spectra were carried out with a HP5989A spectrometer. Elemental analysis was performed by the Analytical Laboratory, Shanghai Institute of Organic Chemistry. GC-MS analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS). *M_n*, *M_w*, and *M_w*/*M_n* values of polymers were determined with an Agilent Technologies PL-GPC 220 High Temperature Chromatograph at 150 °C (polystyrene calibration, 1,2,4-trichlorobenzene as a solvent at a flow rate of 1.0 mL min⁻¹). ¹H and ¹³C NMR data of polymers were obtained by using [D₄]-*o*-dichlorobenzene as solvent at 110 °C. X-ray crystallographic data were collected with a Bruker AXSD8 X-ray diffractometer. Gas chromatography (GC) was performed with an Agilent 7890A instrument with a flame ionization detector (FID). Routine runs were performed with an Agilent 19091S-001 HP-PONA Methyl Siloxane chromatographic column (50 m length, 0.2 mm diameter, 0.5 μm film) with the following program: 50 °C for 10 min, 10 °C min⁻¹ to 150 °C then 10 min. Response factors (or named correction factor) for acetaldehyde was calculated versus heptane. A known mass of acetaldehyde and heptane were added to a volumetric flask, then dissolved in CH₂Cl₂ (10 mL). The solution (0.1–0.2 μL) was then injected into the GC instrument for analysis. The correction factor for acetaldehyde was calculated by using the following equation:

$$\text{correction factor } K = \frac{[(\text{mass of acetaldehyde}) \times (\text{area of heptane})]}{[(\text{mass of heptane}) \times (\text{area of acetaldehyde})]}$$

Materials: Toluene, hexane, CH_2Cl_2 , and THF solutions were purified by using a MB SPS-800 system. Unless otherwise stated, all solvents and reagents were purchased from commercial suppliers and used as received. Ligands **L1**–**L4**^[1b] and $\text{Pd}(\text{OTf})_2 \cdot 2\text{H}_2\text{O}$ ^[20] were synthesized according to known procedures.

General procedure for synthesis of palladium(II) complexes 1–3 and $\text{Pd}(\text{OTf})_2 \cdot 2\text{H}_2\text{O}$:

Complex 1: A solution of diimine **L1** (2.7 g, 5.44 mmol) and $[(\text{COD})\text{PdCl}_2]$ (1.48 g, 5.18 mmol) in CH_2Cl_2 (30 mL) was stirred at RT for one week. The solution was filtered and concentrated, and the solid was washed with CH_2Cl_2 twice and dried under vacuum to afford compound **1** (1.4 g, 40%) as a yellow solid. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ = 8.12 (d, J = 8.4 Hz, 2H), 7.49 (t, J = 6.3 Hz, 4H), 7.36 (d, J = 7.5 Hz, 4H), 6.53 (d, J = 7.2 Hz, 2H), 3.58–3.42 (m, 4H), 1.52 (d, J = 6.6 Hz, 12H), 0.98 ppm (d, J = 6.9 Hz, 12H); elemental analysis calcd (%) for $\text{C}_{36}\text{H}_{40}\text{Cl}_2\text{N}_2\text{Pd}$ (677.64): C 63.77, H 5.95, N 4.13; found: C 63.56, H 5.86, N 4.04.

Complex 2: A solution of $\text{Pd}(\text{OAc})_2$ (0.224 g, 1.0 mmol) and diimine **L1** (0.50 g, 1.0 mmol) in CH_2Cl_2 (15 mL) was stirred at RT for 17 h. The solution was filtered and concentrated. The solid was washed with cold CH_2Cl_2 and dried under vacuum to give the desired compound (0.51 g, 70.3%) as a yellow solid. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ = 8.12 (d, J = 8.4 Hz, 2H), 7.47–7.31 (m, 8H), 6.63 (d, J = 7.2 Hz, 2H), 3.68–3.64 (m, 4H), 1.56 (d, J = 6.6 Hz, 12H), 1.49 (s, 6H), 0.92 ppm (d, J = 6.6 Hz, 12H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ = 176.5, 174.0, 146.8, 140.6, 140.3, 132.7, 131.4, 129.1, 129.0, 125.8, 124.7, 124.3, 29.4, 24.4, 23.7, 22.4 ppm; elemental analysis calcd (%) for $\text{C}_{40}\text{H}_{46}\text{N}_2\text{O}_4\text{Pd}$ (724.76): C 66.25, H 6.39, N 3.86; found: C 66.11, H 6.50, N 3.70.

Complex 3: A solution of AgOTf (3.8 g, 14.8 mmol) and complex **1** (4.8 g, 7.08 mmol) in CH_2Cl_2 (100 mL) was stirred in the dark at RT for 3 h. The solution was filtered and concentrated, and the solid was washed with CH_2Cl_2 twice and dried under vacuum to give the desired compound (4.84 g, 73.8%) as a yellow solid. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ = 8.26 (d, J = 8.7 Hz, 2H), 7.70–7.52 (m, 4H), 7.39 (d, J = 7.5 Hz, 4H), 6.56 (d, J = 7.5 Hz, 2H), 3.70–3.56 (m, 4H), 1.61 (d, J = 6.6 Hz, 12H), 0.98 ppm (d, J = 6.9 Hz, 12H); $^{13}\text{C NMR}$ (100 MHz, $[\text{D}_6]\text{DMSO}$): δ = 179.9, 148.3, 141.0, 138.4, 134.4, 131.1, 131.0, 129.7, 126.1, 125.4, 123.5, 122.2, 119.0, 115.8, 28.8, 23.9, 23.6 ppm; elemental analysis calcd (%) for $\text{C}_{38}\text{H}_{44}\text{F}_6\text{N}_2\text{O}_8\text{PdS}_2$ (940.66): C 48.49, H 4.71, N 2.98; found: C 48.53, H 4.86, N 2.97.

$\text{Pd}(\text{OTf})_2 \cdot 2\text{H}_2\text{O}$: NaOH (4.47 g, 111.8 mmol) and HCOONa (3.93 g, 57.8 mmol) were added to a solution of PdCl_2 (2.24 g, 12.7 mmol) in H_2O (220 mL). Pd sponge was precipitated after stirring for 30 min at RT. The solid was collected and washed with acetone to afford Pd sponge. $\text{CF}_3\text{SO}_3\text{H}$ (42.74 mL) was added at 0°C to a solution of $\text{Pd}(\text{NO}_3)_2$, prepared by dissolving Pd sponge in conc. HNO_3 (3.19 mL). The solution was stirred for 2 h, and the solid was separated by centrifugation and dried under reduced pressure at 110°C for 18 h to give the desired compound (3.8 g, 59%) as light-purple powder. Elemental analysis calcd (%) for $\text{C}_2\text{F}_6\text{H}_4\text{O}_8\text{PdS}_2$ (440.35): C 5.45; found: C 5.74.

General procedure for olefin polymerization:

One-pot process: Ligand (1.5 equiv, 75 μmol) and $\text{Pd}(\text{OTf})_2 \cdot 2\text{H}_2\text{O}$ (1.0 equiv, 50 μmol) were dissolved in DCE (50 mL) and the solution was stirred for ca. 15 min, then ethylene was bubbled into the solution for 6 h at 25°C. The resulting mixture was diluted with petroleum ether, filtered, and concentrated to give polyethylene as a colorless oil.

Typical procedure for water-initiated ethylene polymerization (Table 1, entry 7): H_2O (45 μL) was added to a solution of complex **3** (50 μmol) in CH_2Cl_2 (50 mL), and ethylene was bubbled into the solution for 6 h at 25°C. The resulting mixture was diluted with petroleum ether, filtered, and concentrated to give polyethylene as a colorless oil.

Typical procedure to correlate acetaldehyde and polyethylene (Table 4, entry 1): $\text{Pd}(\text{OTf})_2 \cdot 2\text{H}_2\text{O}$ (8.4 mg) under an ethylene atmosphere was cooled to -78°C , and CH_2Cl_2 (5.0 mL), H_2O (8.4 μL), and CH_2Cl_2 (5.0 mL) were injected sequentially. Ligand **L1** (31 μmol) in CH_2Cl_2 (1.68 mL) was injected and the tube was sealed. The mixture was stirred for 0.5 h at 25°C, then cooled to -78°C . To this solution was added to

heptane (5.3 mg) and the solution was stirred for ca. 5 min at -78°C . Acetaldehyde yields were determined based on GC analysis. After removal of the solvent, the yields of polyethylene were obtained.

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