Olefin Polymerization

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Redox-Controlled Olefin (Co)Polymerization Catalyzed by Ferrocene-Bridged Phosphine-Sulfonate Palladium Complexes

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Abstract: *The facile and reversible interconversion between neutral and oxidized forms of palladium complexes containing ferrocene-bridged phosphine sulfonate ligands was demonstrated. The activity of these palladium complexes could be controlled using redox reagents during ethylene homopolymerization, ethylene/methyl acrylate copolymerization, and norbornene oligomerization. Specifically in norbornene oligomerization, the neutral complexes were not active at all whereas the oxidized counterparts showed appreciable activity. In situ switching between the neutral and oxidized forms resulted in an interesting "off" and "on" behavior in norbornene oligomerization. This work provides a new strategy to control the olefin polymerization process.*

With the development of new polymerization techniques, such as controlled radical polymerization,[1,2] metathesis polymerization,[3] and living coordination polymerization,[4] it is possible to create polymers with almost unlimited structures and functionalities. In most cases, this has been possible through structural modification of the metal catalysts. However, the complexity and cost of chemical synthesis increase exponentially for the generation of new catalysts and correspondingly new polymers. Therefore, the idea of temporally switchable polymerization is highly attractive.[5] The control of catalytic transformations using external stimuli has become an important topic of investigation.[6,7] In such a process, only one catalytic species is employed, and its reactivity can be modulated using external stimuli. For example, Mirkin et al. investigated the control of ε-caprolactone ring-opening polymerization through allosteric control of the catalysts with supramolecular structure.[8] Matyjaszewski et al. reported electrochemically mediated controlled radical polymerization.[9] Manners et al. studied photochemically controlled anionic polymerization using a silicon-bridged ferrocenophane monomer.[10] Sijbsema et al. reported a mechanochemically controlled ring-opening metathesis polymerization using a ruthenium alkylidene complex.[11]

Redox-controlled polymerization has received much attention because of the redox-active nature of many transition-metal complexes and the ease of switching between different redox states. Long, Gibson, and co-workers reported the first example of redox-controlled polymerization (Figure 1; **I**).[12] They showed that the rate of *rac*-lactide ring-opening polymerization could be regulated by changing the redox state of a ferrocenyl unit in a titanium salen catalyst.

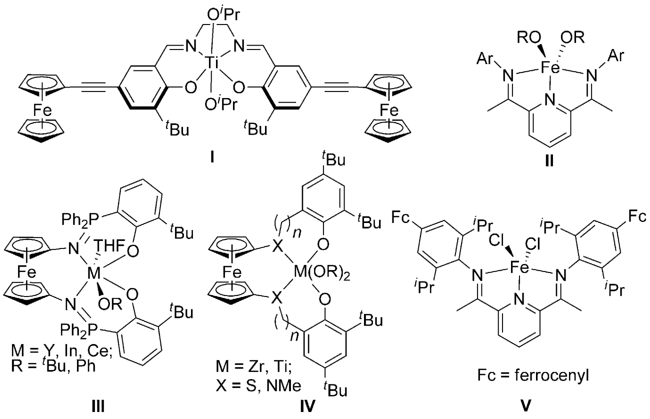

Figure 1. Previously reported redox-active metal catalysts.

Byers et al. studied redox-controlled lactide polymerization catalyzed by bis(imino)pyridine iron bis(alkoxide) complexes (Figure 1; **II**).[13] Diaconescu et al. demonstrated that redox control can be realized in lactide polymerization and copolymerization using several redox-active ferrocene-containing ligands (Figure 1; **III** and **IV**).[14–16] Despite these advances, redox-controlled polymerization has mainly been realized in ring-opening polymerization of cyclic-ester-type monomers such as lactide or ε-caprolactone.

Metal-catalyzed olefin coordination polymerization is a major polymerization technique with great industrial importance. Since the introduction of the Nobel-Prize-winning Ziegler–Natta catalyst, this field has enjoyed tremendous successes both in academia and in industry. Similar with most polymerization techniques, the catalyst is the key in controlling the process. The development of metallocene-type catalysts enabled the synthesis of polyethylene and polypropylene with narrow polydispersity.[17] Constrained geometry catalysts (CGC) made the synthesis of linear low-density polyethylene with well-defined structure possible.[18] Bulky α-diimine Pd catalysts led to chain-walking olefin polymerization and copolymerization with methyl acrylates.[19] Random block copolymers were synthesized by chain-shuttling polymerization using two catalysts and a chain transfer agent.[20] Copolymerization of ethylene with a series of polar monomers was realized using phosphine-sulfonate palladium

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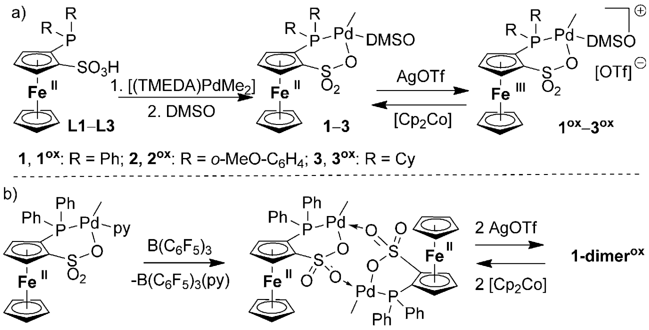
catalysts.[21] All of these successes originated from the discovery or design of new catalysts. However, it becomes more and more difficult, as well as costly, to synthesize new catalysts, and as a result increasingly difficult to discovery new olefin polymerization strategies or new polyolefin materials.

With this in mind, the idea of redox-controlled olefin polymerization is highly fascinating. Gibson et al. studied the redox potentials of ferrocene-containing pyridine-imine Ni and Pd complexes. Unfortunately, no difference between the neutral and oxidized species was detected in ethylene polymerization.[22] The same group studied the ethylene polymerization behavior of neutral and oxidized ferrocene-substituted bis(imino)pyridine iron and cobalt complexes (Figure 1; **V**), which again showed no difference between oxidized and neutral forms. The reducing properties of methylaluminoxane (MAO) and the trialkyl aluminum cocatalyst was proposed to be responsible.[23]

Herein, we report an example of redox-controlled olefin polymerization and copolymerization catalyzed by a series of palladium complexes with ferrocene-containing phosphine sulfonate ligands. This method provides a new strategy to control the olefin polymerization and copolymerization processes, and is an example of redox-controlled polymerization other than ring-opening polymerization of cyclic-ester-type monomers.

The ferrocene-bridged phosphine sulfonate ligands with phenyl and *o*-MeO-C_6H_4 substituents (**L1**, **L2**) were prepared using a reported procedure.[24] The ligand with a cyclohexyl (Cy) substituent (**L3**) was prepared using a similar method. Complexes **1**–**3** were obtained in 65–82 % yields from the reaction of the phosphine sulfonate ligands (**L1**–**L3**) with [(TMEDA)$PdMe_2$] (TMEDA = *N*,*N*,*N′*,*N′*-tetramethyl-1,2-ethane) in dimethylsulfoxide (DMSO) as the solvent using the procedure developed by Mecking et al. (Scheme 1 a).[25]



Scheme 1. a) Synthesis of the neutral (**1**–**3**) and oxidized palladium complexes (**1^{ox}**–**3^{ox}**). b) Synthesis of the neutral (**1-dimer**) and oxidized palladium dimer complexes (**1-dimer^{ox}**). py = pyridine.

Complexes **1**–**3** were characterized using ^1H, ^{13}C, and ^{31}P NMR spectroscopy, as well as elemental analysis and ESI-MS. Electrochemical studies ($E_{1/2}$ versus Ag/AgCl for **1** = 0.839 V, $E_{1/2}$ for **2** = 0.691 V, $E_{1/2}$ for **3** = 0.786 V; see Figure S28–S30 in the Supporting Information) suggested that the commonly used ferrocenium salts ($E_{1/2}$ for [Cp_2Fe][BAr^F] = 0.474 V; Cp = cyclopentadienyl, BAr^F = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) cannot be used to oxidize these palladium complexes. Fortunately, AgOTf ($E_{1/2}$ = 0.904 V) is potent enough to serve as the oxidant. As a control experiment, three benzene-bridged phosphine-sulfonate palladium analogues were prepared and studied. No peak was observed in the electrochemical curves in the 0–2 V range (Figure S32–S34). This suggested that the Pd^{II} center could not be oxidized under the experimental conditions.

NMR analysis showed that the signals attributable to complexes **1**–**3** became very broad and shifted after the addition of 1 equivalent of AgOTf. The addition of another equivalent of AgOTf to the **1**/AgOTf mixture did not result in any changes to the NMR spectrum, suggesting complete oxidation of complex **1** with 1 equivalent of AgOTf (Figure S35). Moreover, the signals for the neutral complexes reappeared with the addition of [Cp_2Co] (Figure S35–S37). The coordination of DMSO to the Pd center was maintained during the oxidation/reduction processes. These results indicated that the oxidation process was facile and reversible (Scheme 1 a). The oxidized species (**1^{ox}**–**3^{ox}**) can be prepared and isolated on large scale (and with yields of 80–88 %) by means of an oxidation reaction between **1**–**3** and AgOTf. The oxidized species (**1^{ox}**–**3^{ox}**) were characterized using ^1H, ^{19}F, and ^{31}P NMR spectroscopy and elemental analysis.

To perform mechanistic studies, the base-free dimer (**1-dimer**) was synthesized from the reaction of the palladium pyridine adduct with 1 equivalent of B(C_6F_5)$_3$, from which **1-dimer** was obtained in 80 % yield (Scheme 1 b). The molecule was characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, elemental analysis, and ESI-MS. Electrochemical studies ($E_{1/2}$ versus Ag/AgCl for **1-dimer** = 0.885 V; Figure S31) suggested that it can be oxidized to **1-dimer^{ox}** using AgOTf. By using NMR experiments to monitor the reaction, the reversible oxidation/reduction of **1-dimer** with AgOTf and [Cp_2Co] was confirmed (Scheme 1 b; Figure S38). Complex **1-dimer^{ox}** was also prepared and isolated in 90 % yield.

The molecular structure of **1-dimer** was determined by X-ray diffraction (Figure 2). The geometry at both palladium centers is square planar, and the methyl group is *cis* to the phosphine. Interestingly, the central eight-membered ring adopts a twisted boat conformation, with both palladium atoms on the axial positions. This is different from previously reported palladium dimer species based on phosphine arene-sulfonate ligands, in which a chair conformation of the eight-membered ring was detected.[26] The (PO)Pd chelate ring is puckered, with one P-Ph group located on a pseudo-axial position and another on a pseudo-equatorial position.

Both the neutral (**1**–**3**) and the oxidized (**1^{ox}**–**3^{ox}**) complexes were highly active as catalysts for ethylene polymerization (Table 1). After oxidation, the activity was decreased four- to sixfold (as indicated by productivity values (*P*) in Table 1), and the polyethylene molecular weight was about 3–5 times lower. The polydispersity index (PDI) of the polyethylene remained narrow for the oxidized complexes (**1^{ox}**–**3^{ox}**), suggesting the presence of only one active species during the ethylene polymerization. Recently, Mecking et al. studied the ligand electronic effects on the ethylene polymerization properties of phosphine-sulfonate palladium complexes, which showed that electron-withdrawing substituents

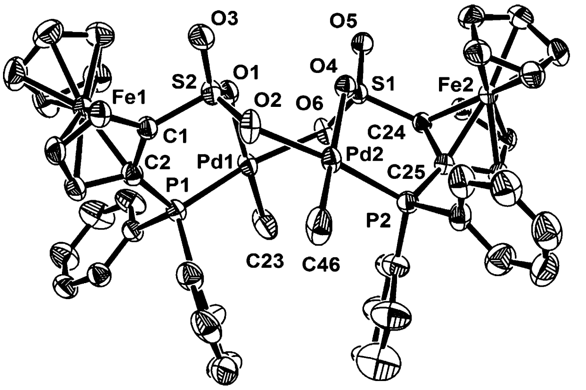


Figure 2. Molecular structure of **1-dimer**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1–O1 = 2.161(4), Pd1–C23 = 2.043(3), Pd1–O6 = 2.185(3), Pd1–P1 = 2.1963(14), S2–O3 = 1.434(5), S2–O1 = 1.460(4), S2–O2 = 1.461(4); O1-Pd1-O6 = 90.93(14), O1-Pd1-P1 = 96.04(10), C23-Pd1-P1 = 87.9(2), C23-Pd1-O6 = 85.8(2) Pd1-O1-S2 = 122.3(2), Pd1-O6-S1 = 128.6(2). Thermal ellipsoids are set at 30% probability.

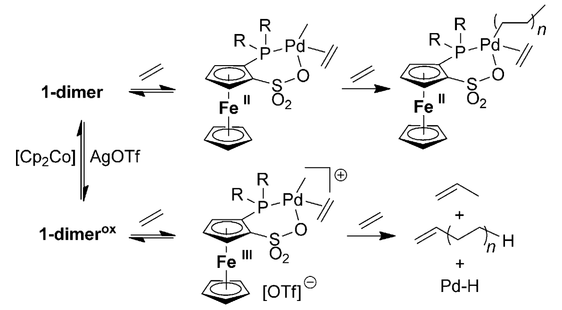
Table 1: Ethylene homopolymerization with **1**–**3** and 1^{ox}–3^{ox}.[a]

Entry	Cat.	Yield [g]	P[b]	T_m [°C][c]	M_n[d]	PDI[d]	B[e]
1	**1**	1.21	4.8	130.9	5860	2.40	5
2	$\mathbf{1}^{ox}$	0.29	1.2	129.6	2050	2.19	8
3	**2**	2.01	8.0	131.7	7830	2.20	6
4	$\mathbf{2}^{ox}$	0.53	2.1	124.2	1420	2.04	13
5	**3**	2.50	10.0	132.1	9760	2.34	5
6	$\mathbf{3}^{ox}$	0.44	1.7	127.7	3290	1.86	8
7[f]	**1**	0.09	3.6	131.2	6510	2.30	5

[a] Polymerization conditions: catalyst (5 μmol), toluene (48 mL), CH_2Cl_2 (2 mL), ethylene (9 atm), 80 °C, 0.5 h. [b] Productivity (P) is in units of 10^5 g mol^{-1} h^{-1}. [c] Determined by differential scanning calorimetry (DSC). [d] Determined by gel permeation chromatography (GPC) using universal calibration. [e] Branching density, B = branches per 1000 carbons, determined by ^{1}H NMR spectroscopy. [f] 0.5 μmol catalyst.

could increase the activity and decrease the polymer molecular weight.[27] Additionally, Jordan et al. showed that the coordination of $B(C_6F_5)_3$ to a phosphine-sulfonate palladium complex could efficiently decrease the electronic density at the palladium center, leading to the increase in both the chain growth rate and the chain transfer rate in ethylene polymerization.[26]

The oxidized ferrocene moiety is electronically more withdrawing than its neutral counterpart, which is probably responsible for the faster chain transfer and correspondingly lower polyethylene molecular weight (M_n) and higher branching density (B; Table 1). However, the reduction in activity was quite surprising. It was hypothesized that the oxidized complexes might not be stable under polymerization conditions (80 °C), which was supported by the observation of small amount of palladium black at the end of the polymerization for the oxidized complexes. Unfortunately, it was not possible to compare the activities at low temperatures, because the neutral complexes **1**–**3** only gave trace amount of polyethylene at room temperature or 50 °C. To probe these issues, mechanistic studies for the reactions of **1-dimer** and **1-dimer**^{ox} with 15 equivalents of ethylene in $CDCl_3$ at room temperature were performed (Scheme 2; Figure S39 and S40). After 2.5 h, 30 % of ethylene was consumed when **1-dimer** was employed, whereas 55 % of ethylene was consumed with **1-dimer**^{ox}, suggesting that the initial activity of the oxidized palladium species is indeed higher than that of the neutral species. For **1-dimer**^{ox}, propene (0.2 equiv), 1-butene (1.7 equiv), 2-butene (0.2 equiv), and higher olefins (1.2 equiv) were detected. In contrast, none of these olefin species were detected when **1-dimer** was employed in the reaction. Instead, the broad resonance signals in the $\delta = 0.6$–1.3 ppm region of the ^{1}H NMR spectrum of the product mixture using **1-dimer** suggested the formation of insertion products of Pd alkyl species.



Scheme 2. Mechanistic studies for the reactivity differences between complexes **1-dimer** and **1-dimer**^{ox} in reaction with ethylene.

The decrease in catalytic activity and increase in polymer branching could also be explained by residual amounts of **1** in $\mathbf{1}^{ox}$ during polymerization (with $\mathbf{1}^{ox}$ being inactive). To rule out this possibility, polymerization was carried out using a lower concentration of catalyst **1** (Table 1, entry 7). The molecular weight and branching density at the lower concentration of **1** were found to be similar to those at the higher concentration (Table 1, entry 1). Therefore, it is reasonable to assume that the catalyst carrying out ethylene polymerization in $\mathbf{1}^{ox}$ is a new catalyst and not residual **1** that results from incomplete oxidation of the catalyst.

These results are fully consistent with the above hypothesis that the electron-withdrawing nature of the oxidized ferrocene moiety is responsible for the fast β-H chain transfer. The resulting Pd-H species are more prone to deactivation and palladium black formation,[28] which explains the low stability and low catalytic activity of the oxidized palladium complexes during ethylene polymerization. Also, the activity changes of complexes **1** and $\mathbf{1}^{ox}$ with time supported this argument. At longer reaction times (1 h and 2 h), the activity differences between **1** and $\mathbf{1}^{ox}$ became bigger (Figure S1), confirming the lower stability of complex $\mathbf{1}^{ox}$.

Both the neutral and the oxidized complexes were capable of copolymerizing ethylene with methyl acrylate (MA; Table 2). Again, the oxidized complexes showed a 2–4 times lower activity and a 1.5–2 times lower MA incorporation (X_{MA}) and lower copolymer molecular weight (M_n). Lower molecular weights were detected in the ethylene/methyl acrylate copolymerization reactions (Table 2) compared to the ethylene polymerization reactions (Table 1). The copoly-

Table 2: Ethylene/methyl acrylate copolymerization with **1**–**3** and 1^{ox}–3^{ox}.[a]

Entry	Cat.	MA [M]	Yield [mg]	P[b]	X_{MA}[c] [%]	M_n[d]	PDI[d]
1	**1**	1.2	180	0.9	5.0	1870	2.56
2	**1**	2.5	150	0.8	12.0	1570	2.30
3	$\mathbf{1}^{ox}$	1.2	58	0.3	3.1	–[e]	–[e]
4	$\mathbf{1}^{ox}$	2.5	36	0.2	8.2	–[e]	–[e]
5	**2**	1.2	1210	6.0	8.8	2730	2.48
6	**2**	2.5	576	2.8	25.0	1600	2.36
7	$\mathbf{2}^{ox}$	1.2	411	2.0	5.0	610	1.66
8	$\mathbf{2}^{ox}$	2.5	139	0.7	10.5	400	1.70
9	**3**	1.2	265	1.3	10	2920	2.75
10	**3**	2.5	213	1.0	18.8	2130	1.78
11	$\mathbf{3}^{ox}$	1.2	87	0.4	6.0	420	1.71
12	$\mathbf{3}^{ox}$	2.5	33	0.2	12.0	330	2.30

[a] Polymerization conditions: total volume of toluene and MA = 48 mL, CH_2Cl_2 (2 mL), catalyst (20 μmol), ethylene (9 atm), 100 °C, 1 h. [b] Productivity is in units of 10^4 g mol^{-1} h^{-1}. [c] X_{MA} = MA incorporation; determined by ^{1}H NMR spectroscopy. [d] Determined by GPC using universal calibration. [e] Molecular weight too small to be accurately determined by GPC.

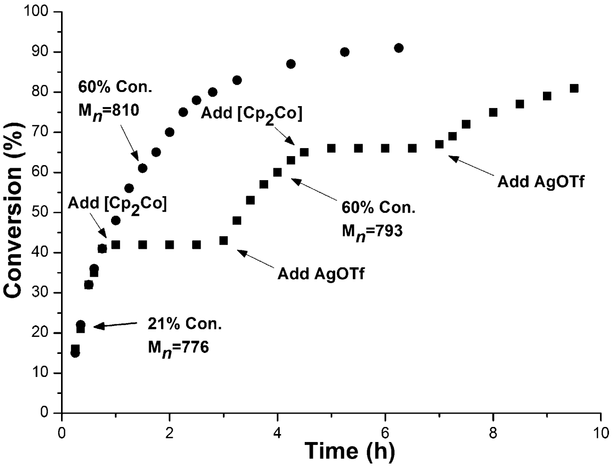


Figure 3. In situ switching oligomerization of NB (100 equiv), starting with the catalyst $\mathbf{3}^{ox}$, in $C_2D_2Cl_4$ at 80 °C. The oligomerization was switched "off" (using [Cp$_2$Co]) and "on" (using AgOTf) twice. The circle symbols (●) correspond to NB oligomerization with catalyst $\mathbf{3}^{ox}$ without switching.

merization behavior of the systems is more easily understood. The palladium center in $\mathbf{1}^{ox}$–$\mathbf{3}^{ox}$ is more electrophilic because of the electron-withdrawing nature of the oxidized ferrocene moiety, making it more prone to MA poisoning, leading to lower activity and lower MA incorporation. The lower stability of the oxidized complexes might also contribute to the lower copolymerization activity. The faster chain transfer ability of the oxidized species resulted in a lower copolymer molecular weight.

The most interesting results came from norbornene (NB) oligomerization. The neutral complexes (**1**–**3**) were not active at all for NB oligomerization, whereas the oxidized counterparts ($\mathbf{1}^{ox}$–$\mathbf{3}^{ox}$) showed appreciable activity. By using NMR experiments to monitor the reactions, it was found that the catalytic activity for complexes $\mathbf{1}^{ox}$–$\mathbf{3}^{ox}$ with NB (100 equiv) in $C_2D_2Cl_4$ at 80 °C followed the order of $\mathbf{3}^{ox} > \mathbf{1}^{ox} > \mathbf{2}^{ox}$ (Figure S53). The in situ switching between the oxidized and neutral forms of the palladium complexes $\mathbf{3}^{ox}$ was investigated for the oligomerization of NB (100 equiv) in $C_2D_2Cl_4$ at 80 °C (Figure 3).

Starting with complex $\mathbf{3}^{ox}$ after 1 h, the oligomerization reached 40 % NB conversion. Upon reduction of complex $\mathbf{3}^{ox}$ with [CoCp$_2$], the oligomerization completely stopped. Once AgOTf was added to the reaction mixture, the oligomerization resumed, and another 30 % of NB conversion was achieved after 1.5 h. The in situ switching can be performed again, at the expense of oligomerization activity. The observed rate constant was indeed decreased after each switching (Figure S55). After a longer "off" time (Figure S56; 4 h versus 2 h at 80 °C), the oligomerization of NB was slower after the switching. These results suggested that catalyst decomposition indeed happened during the course of the oligomerization reaction and in the "off" state.

The NB oligomer obtained from $\mathbf{3}^{ox}$ (1.5 h at 60 % NB conversion, M_n = 810, PDI = 1.90) had a similar molecular weight and a similar molecular weight distribution as those obtained after off/on switching at the same NB conversion rate (2 h total reaction time at 60 % NB conversion: M_n = 793, PDI = 1.84). This suggested that the catalytic system is not living and only one active species exists during each cycle. Similar in situ switching experiments were performed for complexes $\mathbf{1}^{ox}$ and **1-dimer**$^{\mathbf{ox}}$ (Figure S57 and S58).

Recently, we demonstrated that phosphine-sulfonate nickel complexes possessed low activity in norbornene homopolymerization.[29] The binding of $B(C_6F_5)_3$ to sulfonate oxygen can efficiently decrease the electron density at the nickel center and increase the NB polymerization activity by up to 4000 times.[29] A similar mechanism is probably operative in this system. The oxidized form of the ferrocene moiety decreases the electron density at the palladium center, which facilitated the NB binding and the subsequent NB insertion in this system.

To conclude, we described an example of redox-controlled olefin polymerization mediated by metal catalysts. Based on electrochemical and NMR studies of a series of palladium complexes bearing ferrocene-bridged phosphine sulfonate ligands, the interconversion between the neutral and oxidized palladium complexes was shown to be facile and reversible. This work demonstrated that metal-mediated redox control can be applied in polymerization reactions other than ring-opening polymerization of cyclic-ester-type monomers (such as lactide or ε-caprolactone). The oxidized ferrocene moiety efficiently decreases the electron density at the palladium center and facilitates chain transfer during polymerization. This work provides a new and versatile strategy to control olefin polymerization and copolymerization processes.

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[30] CCDC 1416771 (**1-dimer**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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