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Self-Assembled Tetranuclear Palladium Catalysts That Produce High Molecular Weight Linear Polyethylene

Zhongliang Shen and Richard F. Jordan*

Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637

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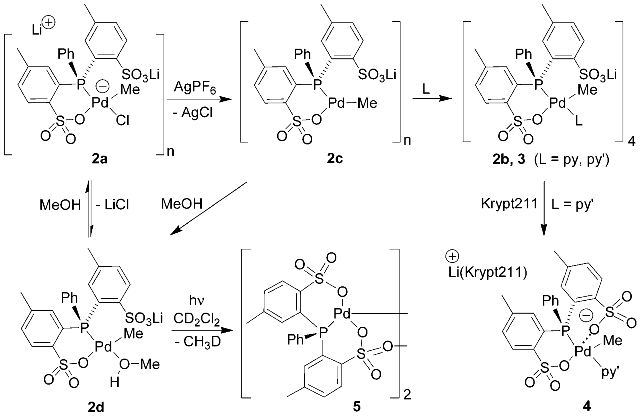
Palladium catalysts based on *ortho*-phosphino-arenesulfonate (PO^-) ligands display interesting olefin polymerization properties. (PO)Pd(R)(L) catalysts (L = labile ligand) polymerize ethylene to linear polyethylene (PE) and copolymerize ethylene with polar vinyl monomers to linear copolymers.[1] However, these catalysts typically exhibit low ethylene polymerization activity ($<100\ g \cdot mmol^{-1} \cdot h^{-1} \cdot atm^{-1}$) and produce PEs with low molecular weights (MWs).[1c] Polar comonomers invariably decrease activities and MWs. Here we describe (PO)Pd(R)(L) catalysts that self-assemble into tetrameric species that produce very high MW PE.

The new ligand $PPh(2\text{-}SO_3Li\text{-}4\text{-}Me\text{-}Ph)_2$ (Li_2[OPO], **1**) reacts with (COD)PdMeCl to yield $\{Li[(Li\text{-}OPO)PdMe(Cl)]\}_n$ (**2a**, Scheme 1). NMR studies show that **2a** undergoes reversible solvolysis in MeOH to form **2d**. The reaction of **2a** with $AgPF_6$ in MeOH followed by recrystallization from MeOH/Et_2O yields the base-free complex **2c**. **2c** dissolves in MeOH to form **2d** and reacts with pyridine (py) to form adduct **2b**. NMR studies show that, in CD_3OD, **2a**,**b**,**d** contain one Pd-coordinated and one free sulfonate group, which exchange rapidly above −20 °C.

2a−**d** are soluble only in solvents such as CH_3OH and H_2O that can solvate the pendant $ArSO_3Li$ group. In order to prepare a more soluble (Li-OPO)PdMe(L) complex, 4-(5-nonyl)pyridine (py′) was used as the ligand L.[2] The reaction of **2c** with py′ in CH_2Cl_2 yields $\{(Li\text{-}OPO)PdMe(py')\}_4$ (**3**), which was isolated by recrystallization from CH_2Cl_2/Et_2O. The solid state structure of **3** (Figure 1) is a cubic assembly of four (Li-OPO)PdMe(py′) units linked by Li−O bonds that form a central $Li_4S_4O_{12}$ cage. The $[Li\text{-}OPO]^-$ ligand acts as a κ^2-P,O chelator to Pd. One oxygen of each Pd-bound $ArSO_3^-$ group (O(3)) and all three oxygens of each non-Pd-bound $ArSO_3^-$ group (O(4)−O(6)) coordinate to Li^+ ions to form the cage. Similar motifs were observed in sulfonate MOFs.[3] The Pd atoms are equivalent but are spatially separated into two pairs. The Pd−Pd distance in each pair (Pd(1)−Pd(1A)) is 6.04 Å. The Pd−*Me* groups lie directly under the py′ ring of the neighboring (Li-OPO)PdMe(py′) unit. The IR spectra ($\upsilon(Ar\mathit{SO_3}^-)$ region) of **2a**−**c** and **3** are very similar, suggesting they have similar structures.

NMR studies show that **3** remains intact in CD_2Cl_2 solution at −10 °C and below. The ^1H NMR spectrum of **3** in CD_2Cl_2 at −10 °C contains two sets of $ArSO_3^-$ resonances, consistent with the solid state structure and in contrast to the spectra of **2a**−**d** in CD_3OD for which fast $ArSO_3^-$ exchange is observed at this temperature. The Pd−*Me* ^1H NMR resonance of **3** (δ −0.48) is shifted >0.6 ppm upfield from the range observed for **2a**−**d** and other (PO)PdMe(py) complexes (δ 0.2 - 0.5), consistent with the anisotropic shielding from the proximal py′ ring expected from the solid state structure. Pulsed field gradient spin−echo (PGSE) NMR data in CD_2Cl_2 show that the hydrodynamic volume of **3** is 1.9 times larger than that of dinuclear $\{(PO\text{-}3,5\text{-}^tBu)PdMe\}_2$ ($(PO\text{-}3,5\text{-}^tBu)^-$ = 2-P(3,5-$^tBu_2$-Ph)$_2$-4-Me-benzenesulfonate) and 3.8 times larger than that of mononuclear (PO-3,5-^{t}Bu)PdMe(py), consistent with a tetrameric structure for **3** in solution.

Scheme 1



As the temperature of a CD_2Cl_2 solution of **3** is raised above −10 °C, a new species (**3′**) grows in reversibly at the expense of **3**. NMR studies show that **3′** is a smaller fragment of **3**, most likely a monomeric (Li-OPO)PdMe(py′) species. The ^1H NMR spectrum of **3′** at 80 °C in $CDCl_2CDCl_2$ contains one $ArSO_3^-$ methyl resonance (δ 2.27), consistent with fast $ArSO_3^-$ exchange as observed for **2a**−**d** in CD_3OD, and a Pd−*Me* resonance (δ 0.46) in the range for monomeric (PO)PdMe(L) species. PGSE NMR data show that the hydrodynamic volume of **3′** is $^1/_3$ to $^1/_4$ that of **3**. The concentrations of **3** and **3′** fit the equilibrium expression for a tetramer/monomer equilibrium, with $K_{eq} = [\mathbf{3'}]^4/[\mathbf{3}] = 9.6(2) \times 10^2\ M^3$ at 80 °C. The entropy value (ΔS = 34(2) eu) is consistent with dissociation of **3** into multiple fragments.

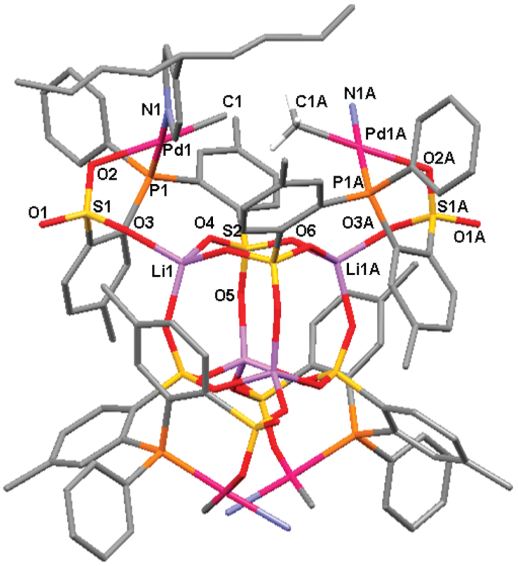


Figure 1. Molecular structure of $\{(Li\text{-}OPO)PdMe(py')\}_4$ (**3**). Hydrogen atoms (except $C(1A)H_3$) are omitted. Only the nitrogen atoms of the N1A-C py′ ligands are shown.

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Table 1. Representative Ethylene Polymerization Results[a]

entry	cat.	P (psi)	T (°C)	time (h)	yield (g)	M_w[e] (10^3)	PDI[e]	T_m[g] (°C)
1[b]	**PO1**	410	80	2	2.84	13.2	2.0	131.4
2[b]	**PO2**	435	80	2	4.36	58.8	2.5	132.9
3[b]	**3**	410	80	2	6.25	7.87	2.6	131.7
4[b]	**2a**	410	80	2	0.85	1110	28	135.4
5[b]	**2b**	410	80	2	4.85	382	49	134.3
6[b]	**2c**	410	80	1	1.35	284	31	134.3
7[c]	**PO1**	410	80	2	0.35	6.39	2.0	129.3
8[c]	**3**	410	80	2	5.18	1000	60	138.7
9[d]	**3**	80	25	24	1.91	915	29	136.5
10[d]	**PO2**	80	25	24	0.45	29.0	2.2	136.3
11[d]	**4**	80	25	24	2.25	oligo[f]	–	–

[a] Solvent = 50 mL, [Pd] = 0.2 mM (10 μmol). [b] Solvent = toluene. [c] Solvent = hexanes. [d] Solvent = CH_2Cl_2. [e] GPC. [f] C_4–C_{18} oligomers. [g] DSC.

The reaction of **3** with the cryptand Krypt211 yields [Li(Krypt211)][(OPO)PdMe(py′)] (**4**). The $[OPO]^{2-}$ ligand of **4** binds to Pd as a κ^2-P,O chelator, and the pendant sulfonate group interacts weakly with the Pd (Pd–O distance: 3.08 Å; sum of van der Waals radii of Pd and O: 3.15 Å). **2d** undergoes Pd–Me bond homolysis in fluorescent room light in CD_2Cl_2 to yield $\{(OPO)Pd\}_2$ (**5**) and CH_3D.[4] The $[OPO]^{2-}$ ligands in **5** act as κ^3-O,P,O pincers to each Pd and also bridge via one SO_3^- oxygen.

In toluene at 80 °C (410 psi ethylene), mononuclear {2-(Ar_2P)-4-Me-benzenesulfonate}PdMe(py) catalysts (**PO1**: Ar = Ph; **PO2**: Ar = 2-Et-Ph) produce linear PE with low to moderate MW and a narrow molecular weight distribution (MWD; Table 1, entries 1,2), characteristic of single site catalysis. **3** behaves similarly (entry 3). Under these conditions, **PO1** and **PO2** are completely soluble and **3** is highly soluble. In contrast, **2a–c** produce very high MW linear PE with a broad bimodal MWD (entries 4–6 and Figure 2a), suggestive of multisite catalysis. The insoluble **2a** yields PE with a large high MW fraction, while sparingly soluble **2b**,**c** yield PEs with a large low MW fraction.

To explore the influence of catalyst solubility, the polymerization behaviors of **PO1** and **3** were compared under homogeneous and heterogeneous conditions. **PO1** behaves similarly in toluene (initially homogeneous) and hexanes (heterogeneous) except that the MW decreases slightly in hexanes (Table 1, entries 1,7). In contrast, **3** generates low MW PE with a narrow MWD in toluene (as noted above) but produces high MW PE with a broad MWD and a significant high MW component in hexanes (entries 3,8, and Figure 2b). These results show that the solubility of the catalyst *per se* does not control the MW but rather suggest that the nuclearity of the catalyst is a key factor. That is, under heterogeneous conditions (hexanes), **3** substantially maintains its tetranuclear structure (as shown by X-ray diffraction) and produces high MW PE. However, in solution (toluene), **3** and/or growing higher-alkyl analogues break up to form mononuclear species (as shown by NMR) that produce low MW PE, similar to conventional (PO)Pd(R)(L) catalysts. The overall MWD is broad and reflects the degree of cage fragmentation under the given polymerization conditions. Similar reasoning explains the behavior of **2a–c**. This proposal is supported by the polymerization behavior of **3** in CH_2Cl_2 at 25 °C. Under these conditions, **3** is initially completely soluble and 90% intact and produces PE that contains a substantial high MW component (entry 9). The broad MWD is again due to fragmentation of **3** and/or growing higher-alkyl analogues. The lower temperature disfavors fragmentation, but this effect may be counteracted by the higher polarity of the solvent (ϵ: CH_2Cl_2, 8.9; toluene, 2.4).

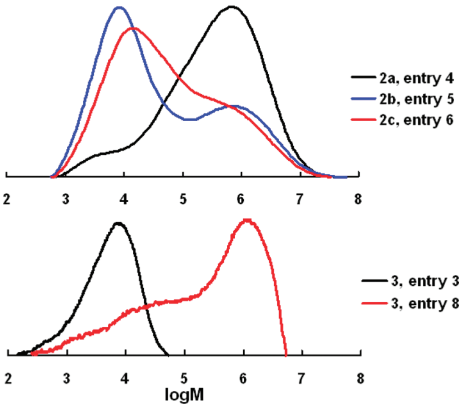

Figure 2. GPC traces of PE samples obtained from (a) **2a**, **2b**, and **2c** in toluene at 80 °C and (b) **3** in toluene and hexanes at 80 °C. See Table 1.

Surprisingly, **4** produces only ethylene oligomers (Table 1, entry 11) in good yield. The oligomers display a Schulz–Flory distribution ($\beta = 0.69$), consistent with single site catalysis. These results show that a pendant free $ArSO_3^-$ group strongly enhances chain transfer.

This work shows that the incorporation of the pendant $ArSO_3Li$ group in (Li-OPO)PdMe(L) catalysts dramatically influences their ethylene polymerization behavior. (Li-OPO)PdMe(L) complexes self-assemble into tetranuclear species that produce very high MW PE. In solution, the tetramers fragment into mononuclear species that behave like normal (PO)Pd(R)(L) catalysts and produce low MW PE. When the Li^+ counterion is sequestered by a cryptand, only ethylene oligomers are formed. The unusual production of a high MW polymer by the tetranuclear species may result from steric effects. The crystal structure of **3** shows that one axial face of the Pd center is blocked by the $Li_4S_4O_{12}$ cage, which may disfavor associative chain transfer.[5] It is also possible that cooperative effects between the Pd centers in **3** are important.[6] The free $ArSO_3^-$ group in **4** may facilitate chain transfer by displacing the olefin in Pd(H)(olefin) intermediates generated by β-H elimination or by stabilizing the transition state for β-H transfer to monomer by coordinating to Pd. We are exploring multinuclear catalysts based on more robust self-assembled cages.

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Supporting Information Available: Experimental procedures and characterization of complexes (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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