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Ruthenium(IV) Complexes for Ethylene Insertion Polymerization

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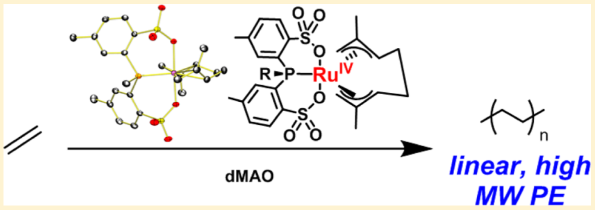
S *Supporting Information*

ABSTRACT: The synthesis, characterization, and ethylene polymerization behavior of novel $Ru^{IV}(\eta^3:\eta^3\text{-}C_{10}H_{16})(OPO)$ (OPO = bis(arenesulfonato)phosphine) complexes is reported here. Upon activation with $AlMe_3$-depleted methylaluminoxane (dMAO), the Ru(IV) precursors were able to produce polyethylene with activities up to 1182 h^{-1} turnover frequency (TOF). The polymers were highly linear with a low degree of branching (<12 methyl branches per 1000 C) and had high molecular weights (up to M_p = 289 kg mol^{-1}) with a bimodal molecular weight distribution. The polymerization activity increased with decreasing donor strength of the OPO ligand.



Billions of pounds of polyolefins are produced annually to serve various applications, including plastics, elastomers, and fibers.[1] The design of novel olefin polymerization catalysts remains at the frontier of polyolefin technology.[2] Traditionally, the heterogeneous Ziegler−Natta catalysts[3] and homogeneous metallocene catalysts[2a,d,4] for olefin insertion polymerization are based on early-transition-metal (early-TM) complexes with high oxidation states.[5] More recently, the potential of late-TM catalysts for olefin polymerization has been explored. While Ni-based oligomerization catalysts have been employed industrially in the Shell Higher Olefins Process (SHOP),[6] the introduction of bulky diimine ligands to Ni(II) and Pd(II) complexes resulted in the first successful late-TM polymerization catalysts in the mid-1990s.[7] This discovery by Brookhart and co-workers has sparked tremendous interest in the olefin polymerization community and led to the development of several highly active late-TM catalyst systems. For example, Fe and Co complexes of bulky diiminopyridine ligands were shown to exhibit polymerization activities comparable to those of the most active Ziegler−Natta catalysts.[8] Active neutral Ni^{II}(salicylaldiminato) complexes were also reported for ethylene homo- and copolymerizations.[9] In addition, late-TM catalysts are less sensitive toward polar functionalities. This tolerance has been exploited to obtain copolymers of various polar olefins with neutral palladium catalysts coordinated to *o*-phosphinobenzenesulfonate ligands.[10]

Ruthenium complexes have shown great versatility as catalysts for various transformations, most notably for hydrogenation[11] and olefin metathesis reactions.[12] The high affinity for olefin binding combined with good functional group tolerance for Ru complexes[13] makes them desirable for developing new olefin polymerization catalysts. Nevertheless, despite the high activity of Fe^{II}(diiminopyridine) catalysts,[8] surprisingly few Ru-based olefin insertion polymerization catalysts have been reported. In addition to sporadic uses of Ru^{II}−hydrides for olefin polymerization[13] and direct and indirect demonstrations of ethylene insertion into Ru^{II}−hydride, −aryl, and −alkyl bonds,[14] Nomura and co-workers[15] first reported the synthesis of high-molecular-weight polyethylene with a Ru^{II}(pybox) complex. However, Brookhart and co-workers later showed that an analogous Ru^{II}(diiminopyridine) system was inactive for ethylene polymerization. Furthermore, they were able to obtain the putative active species of their system, the $[Ru^{II}(\text{diiminopyridine})Me(C_2H_4)]^+$ cation, which was inactive toward migratory insertion of ethylene.[16] The authors proposed that the meridional coordination geometry of the ligand results in distinctly different coordination sites for the coordinated ethylene and alkyl group (*cis* and *trans* to pyridine), which makes alkyl migration energetically unfavorable. A computational study calculated the insertion barriers for this system to be >25 kcal mol^{-1}, which is conceivably too high for active ethylene polymerization.[17] More recently, a neutral Ru(II) complex containing two *o*-phosphinobenzenesulfonate ligands was reported to exhibit relatively low activity toward ethylene polymerization.[18] Surprisingly, the obtained polymer was found to be chemically cross-linked. Similar to Ru, reports on Rh complexes for olefin polymerization are also rare.[19]

Recently, our laboratory has unambiguously demonstrated for the first time the insertion polymerization of ethylene by a ruthenium metal center.[20] The thioether-tethered Ru^{II}(arene) complex produced polyethylene with relatively low activity. We reasoned that Ru complexes with higher oxidation states should lead to an increase in the catalyst activity analogous to early TM. Ru(IV) was chosen due to its diamagnetic nature, facilitating NMR spectroscopic characterization. We employed bis(arenesulfonato)phosphine (OPO) ligands to stabilize the Ru(IV) center. The OPO ligand motif was first reported by Jordan and co-workers[21] as a bidentate ligand for Pd(II) complexes for ethylene polymerization. The dianionic ligand was envisioned to chelate the Ru(IV) center, which upon activation could afford a monocationic Ru^{IV}−alkyl complex as

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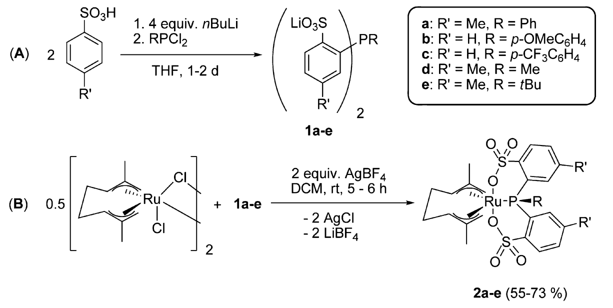
the active catalytic species for olefin insertion polymerization. In this report we describe the synthesis and characterization of a series of Ru^{IV}(OPO) complexes and their ethylene polymerization behavior upon activation with aluminum alkyl cocatalysts.

The ligand **1a** was synthesized following the literature procedure.[21] A series of novel Li_2(OPO) ligand variants (**1b**−**e**; Scheme 1) were synthesized by treating the respective phosphine dichloride with 2 equiv of *o*-lithioarenesulfonate (see the Supporting Information for all ligand syntheses and characterizations). To tune the catalytic properties of the Ru(IV) complexes, the substituent on the phosphine was systematically changed, including three phenyl variants with different electronic properties (**1a**−**c**) and two alkyl substituents with different steric bulk (**1d**,**e**). The structures of all the ligands were fully established by ^1H and ^{13}C NMR, ESI-MS, and elemental analysis (see the Supporting Information). The solid-state structure of **1c** was determined by X-ray diffraction analysis (see Figure S40 in the Supporting Information).

Scheme 1. Synthesis of (A) Li_2(OPO) Ligands 1 and (B) Ru(IV) Polymerization Precatalysts 2



Treating the Ru(IV) dimer $[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ with **1** in the presence of $AgBF_4$ resulted in the formation of neutral $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(OPO)]$ complexes **2** in 55−73% yield after purification (Scheme 1). All complexes were characterized by ^1H and ^{13}C NMR, ESI-MS, and elemental analysis (see the Supporting Information). High-quality single crystals of **2d**,**e** were obtained, enabling us to determine their solid-state structure by X-ray diffraction analysis (see Figure 1). Both complexes show a trigonal-bipyramidal coordination of the Ru center. The sum of the bond angles of the phosphorus and the central allyl carbon atoms around the ruthenium center was 360.0° in both cases. The OPO fragment was coordinated meridionally with the phosphorus and the dienyl group occupying the equatorial positions and the sulfonates residing in the axial positions. The allyl methyl groups adopted an anti configuration with respect to the equatorial plane. In **2e** the Ru−P bond is elongated to 2.493 Å in comparison to 2.392 Å for **2d**, and the $Ru-P-C_{alkyl}$ angle widened from 123.8° to 131.4° due to the larger steric profile of the *tert*-butyl group. The solid-state structures agreed with the solution structures as determined by NMR spectroscopy. In **2**, the allyl groups gave rise to nonequivalent NMR resonances. For example, in **2d** the allyl methyl signals showed chemical shifts of 1.42 and 2.24 ppm, respectively. Presumably, the ring current effect of the arenesulfonates experienced by the allyl group facing away from the phosphine alkyl moiety leads to an upfield shift of its resonance. A 1D NOE NMR experiment enabled the absolute assignment of the dienyl resonances for **2d.** When P-Me was irradiated, we only observed NOE enhancement for the terminal methylene protons of the downfield-shifted allyl group (see Figure S26 in the Supporting Information).

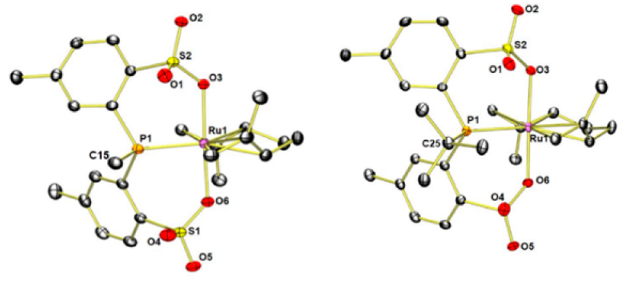


Figure 1. Ortep plots of **2d** (left) and **2e** (right). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) for **2d**: Ru1−O6 2.1132(11), Ru1−O3 2.0953(11), Ru1−P1 2.3919(4); Ru1−P1−C15 123.81(6), O3−Ru1−P1 93.05(3), O6−Ru1−P1 89.50(3). Selected bond distances (Å) and angles (deg) for **2e**: Ru1−O6 2.1124(17), Ru1−O3 2.0998(17), Ru1−P1 2.4931(6); Ru1−P1−C25 131.42(8), O3−Ru1−P1 92.42(5), O6−Ru1−P1 89.43(5).

Complexes **2** were active for ethylene insertion polymerization when treated with $AlMe_3$-depleted methylaluminoxane (dMAO) in toluene at elevated temperatures under optimized conditions (Table 1 and Table S1 in the Supporting Information). Activation with normal MAO gave lower activity in comparison to dMAO while producing polymers with similar properties (run 9 vs 11). The catalyst system **2**/dMAO showed relatively high thermal stability with optimal activities at polymerization temperatures between 55 and 85 °C. The highest TOF (1182 h^{-1}) was obtained with **2c** (run 7), which, to the best of our knowledge, represents the most active Ru-based ethylene polymerization catalyst system reported to date. While this activity is significantly lower than those of highly active Ni(II) and Fe(II) complexes (vide supra), it is one order of magnitude higher than those for other previously reported Ru-based systems.[15,20]

A consistent trend was observed for the donor strength of OPO ligands on catalyst activity. Comparing **2a**−**c** (runs 1, 3, and 8) showed an increase in activity with decreasing donor strength of the ligand. The most electron-rich species, **2b**, produced only trace amounts of polymer. However, it is difficult to directly compare the aryl-substituted (**2a**−**c**) and alkyl-substituted (**2d**,**e**) complexes, as the sterics for the two systems are significantly different. For example, alkyl-substituted **2d**,**e**, containing electron-rich phosphines, gave higher activities than **2a**,**b**. The steric profile of **2e** had a pronounced influence on the polymer properties such as molecular weight (vide infra).

The effects of polymerization time (runs 6−9) and temperature (runs 4, 5, 9, and 10) were investigated in more detail with the most productive **2c**/dMAO system. In experiments with varying reaction time under otherwise identical conditions, the significantly higher productivity (TOF of 1182 h^{-1}) for the 2 h in comparison to that for the 1 h polymerization (runs 6 and 7) suggests a slow activation of **2c**. The decrease in TOF for much longer times (runs 8 and 9) was presumably due to catalyst deactivation with time. For temperature dependence, under otherwise identical conditions, the highest activity was observed at 85 °C. Presumably, initial increase of temperature (runs 4, 5, and 9) accelerated the catalyst activation and increased the insertion rate until catalyst deactivation became more dominant at overly high temperature (105 °C). The optimal temperature for maximum productivity is also ligand dependent; while **2c**

Table 1. Ethylene Homopolymerization Results[a]

run	catalyst	T (°C)	t (h)	yield (mg)	TOF[b]	T_m (°C)[c]	X (%)[d]	M_p (kg/mol)[e]	N_{br}[g]
1	**2a**	80	4	72	64	129	63	257, 0.9[f]	11
2	**2b**	60	4	tr	N/A	n.d.	n.d.	n.d.	n.d.
3	**2b**	80	4	tr	N/A	n.d.	n.d.	n.d.	n.d.
4	**2c**	40	17	120	25	128	37	28, 0.8[f]	6
5	**2c**	60	17	788	165	134	57	289, 0.9[f]	3
6	**2c**	85	1	99	353	135	56	179, 0.7[f]	2
7	**2c**	85	2	663	1182	133	62	153, 0.7[f]	5
8	**2c**	85	4	835	744	135	59	214	1
9	**2c**	85	17	934	196	133	60	190, 1.1[f]	5
10	**2c**	105	17	115	24	128	49	155, 0.8[f]	11
11[h]	**2c**	85	17	519	109	135	58	174, 0.6[f]	5
12	**2d**	55	17	790	166	122	*i*	250, 0.6[f]	9
13	**2d**	85	4	228	203	134	58	219, 0.7[f]	2
14	**2e**	85	4	72	64	131	42	250	n.d.
15	**2e**	95	4	201	179	129	37	250	12
16[j]	**2e**	85	17	0	0	N/A	N/A	N/A	N/A
17	**1c**	85	17	0	0	N/A	N/A	N/A	N/A
18	**1cH**[22]	85	17	0	0	N/A	N/A	N/A	N/A

[a] Conditions: 10 μmol of catalyst, 1000 equiv of dMAO, 600 psi of C_2H_4, 100 mL of toluene. [b] In units of (mol of C_2H_4)/((mol of [Ru]) h). [c] Determined by DSC. [d] Crystallinity measured from DSC traces. A melting enthalpy of 293 J/g was used for 100% crystalline PE.[23] [e] Peak molecular weights (M_p) determined by GPC in 1,2,4-trichlorobenzene at 140 °C vs polyethylene standards. [f] Bimodal molecular weight distribution. [g] Methyl branches per 1000 C. Determined by ^1H NMR in tetrachloroethane-d_4 at 130 °C. [h] MAO as cocatalyst (Al/Ru = 1000). [i] Very broad melting endotherm hampers calculation of crystallinity. [j] Without dMAO cocatalyst.

exhibited maximal productivity at 85 °C, **2d** showed the highest productivity at 55 °C (runs 5 and 9 vs 12 and 13).

The cis diallyl groups in **2** are ideally suited to be activated to form two active coordination sites in cis positions. Nevertheless, numerous attempts to use solution NMR to elucidate the activation mechanism for **2** proved to be elusive due to severe solubility issues encountered when species of **2** were activated by dMAO. On the other hand, small-molecule activators, such as $AlMe_2Cl$, Al(*i*Bu)$_3$, $B(C_6F_5)_3$, and $[Ph_3C]$ $[B(C_6F_5)_4]$/Al(*i*Bu)$_3$, were ineffective for activating **2**. Solution NMR experiments showed no reaction of **2** with excess $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$. This agrees with other reports of Ru(IV) allyl complexes that show no nucleophilic reactivity.[22] Regardless, on the basis of our control experiments (Table 1, runs 16−18), the observed activity was due to the Ru metal center involved in the catalytic process. Polymerization runs without Ru source or cocatalyst yielded no polymer under otherwise identical conditions. Similarly, when ligand salt **1c** or protonated ligand **1cH**[24] was employed with dMAO, no polymer was obtained. This also indicates that the observed polymerization activity was not due to Al/ligand complexes possibly present in the polymerization solution. However, it is possible that the Al cocatalysts undergo redox processes with transition metals, giving active species that differ in their oxidation state from the precatalyst.[25]

The molecular weight and distribution for the polyethylenes obtained in this study were characterized by gel permeation chromatography (GPC). Interestingly, most polymers show bimodal molecular weight distributions (MWD) (see Figures S34−S39 in the Supporting Information for representative traces) with a low- (M_p = 0.6−1.1 kg mol^{-1}) and high-molecular-weight fraction (M_p = 28−289 kg mol^{-1}). The relatively narrow polydispersity index (M_w/M_n = 1.3−3.2) of the monomodal distributions suggests that each active species acts as a single-site catalyst. The molecular weight and the ratio of the two different mass fractions changed with polymerization temperature, time, cocatalyst loading, and precatalyst. The formation of two different types of polyethylene suggests the existence of two different catalytic species in the polymerization solution. This could potentially result from different catalyst activation pathways or complicated interactions of the active metal species with the aluminum cocatalyst (e.g., formation of different ion pairs or heterobimetallic species) which has been reported for other catalysts.[20,26] Chain transfer to dMAO is another potential pathway to give bimodal MWD which was investigated by varying the cocatalyst loading (see Table S1 in the Supporting Information).[8a] The polymerization activity increased with increasing cocatalyst loading and leveled off at an Al/Ru ratio of ∼1000. The polymer obtained with Al/Ru = 500 was of low molecular weight (M_p = 1.3 kg mol^{-1}), while 2000 equivalents of dMAO gave mainly high molecular weight polymer (M_p = 404 kg mol^{-1}). This suggests that chain transfer to Al cocatalyst is unlikely to play a significant role, since it is expected that an increase in Al/Ru ratio leads to a decrease in MW.

All polymers obtained were fully soluble in tetrachloroethane at elevated temperatures. The ^1H NMR spectra revealed that the polymers were highly linear with low degrees of branching (<12 Me branches/1000 C) and contained unsaturated end groups (see Figures S30 and S31 in the Supporting Information). The high terminal olefinic content suggests that β-hydride elimination was a major mode of chain transfer during the polymerization.

The melting temperature (T_m) and crystallinity of the polyethylenes were measured by differential scanning calorimetry (DSC, see Figures S32 and S33 in the Supporting Information). All of the polymers were semicrystalline solids with high T_m values ranging from 129 to 135 °C (except for run 12 with 122 °C and a very broad melting transition).

In conclusion, we report the first Ru(IV) complexes that are active for ethylene insertion polymerization upon activation with dMAO. The polymerization activity for the **2c**/dMAO system is one order of magnitude higher than that for the most active Ru insertion polymerization catalyst reported previously. The polymerizations produce highly linear, semicrystalline polyethylenes with a bimodal molecular weight distribution. It was observed that the catalyst productivity increased with decreasing donor strength of the OPO ligand. Efforts on the development of other ligands and Ru complexes to further improve the catalyst performance are currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Figures, tables, text, and CIF files giving general consideration and materials for the experiments, ethylene polymerization procedure, ligand and complex syntheses, NMR spectra, polymer characterization, X-ray data collection, structure solution, and refinement details and crystallographic data for **1c** and **2d**,**e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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