Selective Ethylene Oligomerization with *In-Situ*-Generated Chromium Catalysts Supported by Trifluoromethyl-Containing Ligands

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ABSTRACT: A series of pyrrole-containing diarylphosphine and diarylphosphine oxide ligands were prepared. The catalytic activity of the corresponding *in-situ*-generated chromium catalysts was investigated during selective ethylene oligomerization reactions. Variations in the ligand system were introduced by modifying the diarylphosphine and pyrrole moieties that affect the steric and electronic properties. Minor changes in the ligand structure and the composition of activators significantly changed the catalytic activity, selectivity toward linear alpha-olefins (LAO) versus polyethylene (PE), and the distribution of oligomeric products. The presence of trifluoromethyl groups on the diphenyl rings in ligand **3** promoted oxidation to form the corresponding phosphine oxide structure, **3o**, which dramatically enhanced the catalytic activity of ethylene trimerization. The *in-situ*-generated chromium complex based on **3o** activated by DMAO (dry methylaluminoxane)/TIBA (triisobutylaluminum) was used to achieve activity of about 1250 g (mmol of Cr)$^{-1}$ h^{-1} with 98.5 mol % 1-hexene, along with a negligible amount of PE side product. © 2017 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2018**, *56*, 444–450

KEYWORDS: catalysts; 1-hexene; α-olefins; oligomers; polyethylene

INTRODUCTION The selective oligomerization of ethylene to 1-hexene and 1-octene is one of the most exciting advancements in olefin catalysis in the past few decades.[1–3] Traditionally, the oligomerization of ethylene by alkyl aluminum or transition metal catalysts follows the Cossee–Arlman mechanism, yielding a Schulz–Flory distribution of oligomers that must be separated by distillation. However, trimerization to 1-hexene or tetramerization to 1-octene provides a selective route to these valuable reagents,[4] which are comonomers for linear low-density polyethylene (LLDPE) production. For this reason, many selective ethylene trimerization and tetramerization catalysts have been developed based on chromium and other transition metals.[1,2,5]

The combination of nitrogen (N) and phosphorus (P) donor atoms within an ancillary ligand system for selective oligomerization has been expanded since the discovery of chromium bis(diphenylphosphino)amine.[1,2,5–7] Although a variety of amine groups on the aminophosphine ligands were extensively studied for selectivity control,[7–10] previous studies on the modification of diarylphosphine parts are quite limited.[11–13] One such study, by Wass and coworkers , claimed that the *ortho*-methoxy-substituted aryl group on bis(diarylphosphino)amine played an important role in the ethylene trimerization and is essential for catalytic activity.[14,15] Sasol Technology also reported that related Cr-diphosphinoamine systems containing alkyl or methoxy substituents in the ortho position of the aryl groups favor trimerization over tetramerization, supporting that *ortho*-substitution at the diarylphosphines is key to switching between tetramerization and trimerization.[16] As far as we know, modification on the diarylphosphines of other P,N-ligand scaffolds has not yet been investigated.

Moreover, phosphine oxides are also important but have received much less attention. They are often considered a sign of incomplete exclusion of oxygen when the corresponding phosphines are the target of synthesis. As far as we know, aminophosphine oxide has not yet been investigated as a ligand for chromium-catalyzed selective ethylene oligomerization.

Recent studies by Yang *et al*. on chromium complexes that are stabilized by a simple N-pyrrolyldiphenylphosphine ligand system showed its versatility for the selective formation of

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1-hexene and 1-octene.[17] We modified the diarylphosphine moiety by introducing methyl or trifluoromethyl groups to study how the substituted diarylphosphine affects catalytic behavior during selective ethylene oligomerization. Herein, we report a catalytic system that has a high activity and selectivity for 1-hexene (up to 99% purity) with only minor by-products. The influence of ligands and activators was systematically studied under various reaction conditions.

EXPERIMENTAL

General Considerations

All oligomerizations were carried out under an N_2 atmosphere using a glove box or by using standard Schlenk techniques, except column chromatography at ambient conditions. All solvents were dried and distilled prior to use according to standard methods. Methylaluminoxane (MAO; 10 wt % in toluene) was purchased from Albemarle Corp. (Baton Rouge, LA, USA). TIBA, pyrrole, 2,4-dimethylpyrrole, 2,5-dimethylpyrrole (DMP), triethylamine, tetrahydrofuran (THF), and nonane were purchased from Sigma-Aldrich (St. Louis, MO, USA). Chlorodiphenylphosphine, chlorodi(*p*-tolyl)-phosphine, bis(3,5-di(trifluoromethyl)phenyl)chlorophosphine, and methylcyclohexane were purchased from Alfa-Aesar (Haverhill, MA, USA). $Cr(acac)_3$ and $CrCl_3(THF)_3$ were used as purchased from Strem Chemicals (Newburyport, MA, USA). Hexane, ethyl acetate, methanol, and hydrogen peroxide (34.5 wt % aqueous solution) were purchased from Samchun Pure Chemical Co. (Korea).

The ^1H NMR spectra of the products were recorded at 25 °C on a Fourier 300 NMR spectrometer (Bruker, Billerica, MA, USA) with tetramethylsilane (TMS) as an internal reference. The ^{13}C NMR spectra and ^{31}P NMR spectra of the products were recorded at 25 °C with Avance III 600 equipment (Bruker) and using TMS as an internal reference. The oligomers (liquid products) were analyzed by gas chromatography with a flame ionization detector (GC-FID) using Agilent 6890 (Agilent Technologies, Santa Clara, CA, USA) equipment with an Agilent J&W GC capillary column, with nonane used as the internal standard. X-ray crystal data were obtained using a SMART APEX II (Bruker) single-crystal X-ray diffractometer equipped with a Bruker SMART charge-coupled device (CCD) area detector. Mass spectra were recorded with a Bruker micrOTOF-QII (ESI) spectrometer.

General Procedure for Ligand Synthesis

Pyrrole (1.4 mL, 20 mmol), Et_3N (2.8 mL, 20 mmol), and THF (6 mL) were charged to a Schlenk flask under an inert atmosphere. Subsequently, chlorodiphenylphosphine (0.85 mL, 4.6 mmol) was added dropwise at 0 °C. The reaction mixture was stirred for 10 min at 0 °C, and for 10 min at room temperature, and then heated to reflux for a further 15 h. The colorless precipitate that formed was removed by filtration and washed with THF. The combined filtrates were evaporated to dryness under vacuum. The resulting oil was re-dissolved in hexane and filtered. The solvent was removed under vacuum to give a crude product, which was purified as described below.

1: Diphenyl(1H-Pyrrol-1-yl)Phosphine

Following the general synthesis, the crude product as a yellow oil was purified by column chromatography, with ethyl acetate:hexane (1:9) used as the eluent. The solvent was removed under vacuum to give the product as a white solid (0.266 g, 0.99 mmol, 21.7%). ^1H NMR (300 MHz, $CDCl_3$, δ): 6.32 (dd, $J = 3.8$, 1.9 Hz, 2H), 6.82 (td, $J = 3.8$, 1.9 Hz, 2H), 7.23–7.31 (m, 4H), 7.38 (d, $J = 3.4$ Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$, δ): 111.62, 125.64, 128.76, 129.86, 132.10, 137.14; ^{31}P NMR (242 MHz, $CDCl_3$, δ): 47.79; purity = 98% on the basis of ^{31}P NMR analysis. HRMS (ESI, m/z): $[M + H]^+$ calcd for $C_{16}H_{15}NP$, 252.0942; found, 252.0930.

2: 1-(Di-p-Tolylphosphino)Pyrrole

Following the general synthesis, pyrrole (0.31 mL, 4.4 mmol), Et_3N (0.62 mL, 4.4 mmol), and chlorodi(p-tolyl)phosphine (0.22 g, 1 mmol) were used. The crude product as a white oil was purified by column chromatography on silica gel, with ethyl acetate:hexane (1:9) as the eluent. The solvent was removed under vacuum to give the product as a white solid (0.09 g, 0.32 mmol, 33.7%). Single crystals were obtained by slow diffusion of hexane into a concentrated solution of the product in THF at room temperature. ^1H NMR (300 MHz, $CDCl_3$, δ): 2.36 (s, 6H), 6.29 (dd, $J = 3.6$, 1.7 Hz, 2H), 6.81 (dt, $J = 3.8$, 2.0 Hz, 2H), 7.14–7.20 (m, 8H); ^{13}C NMR (150 MHz, $CDCl_3$, δ) 21.50, 111.36, 125.50, 129.52, 132.15, 133.93, 139.98; ^{31}P NMR (242 MHz, $CDCl_3$, δ): 47.78; purity = 94% on the basis of ^{31}P NMR analysis. HRMS (ESI, m/z): $[M + H]^+$ calcd for $C_{18}H_{19}NP$, 280.12551; found, 280.1263.

3: Bis(3,5-Bis(Trifluoromethyl)Phenyl)(1H-Pyrrol-1-yl)Phosphine

Following the general procedure, pyrrole (4.4 mmol), Et_3N (0.63 mL, 4.5 mmol), and bis(3,5-(trifluoromethyl)phenyl)-chlorophosphine (0.49 g, 1 mmol) were used. The crude product (**3**) was recrystallized in hexane to yield an ivory solid, which was isolated and characterized immediately. ^1H NMR (300 MHz, $CDCl_3$, δ): $\delta = 6.45$ (dd, $J = 1.8$ Hz, 2H), 6.81 (dd, $J = 3.6$, 1.8 Hz, 2H), 7.66 (d, $J = 6.6$ Hz, 4H), 7.97 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 114.12, 123.0 (q, $^1J_{C-F} = 273$ Hz), 124.58, 125.33, 131.82, 132.81, 139.36; ^{31}P NMR (242 MHz, $CDCl_3$, δ): 42.55; purity = 93% on the basis of ^{31}P NMR analysis.

3o: Bis(3,5-Bis(Trifluoromethyl)Phenyl)(1H-Pyrrol-1-yl)Phosphine Oxide

The product **3** was purified by column chromatography on silica gel, with ethyl acetate:hexane (1:9) as the eluent. On recrystallization from hexane, a white solid was obtained, which was isolated and dried under vacuum (0.17g, 0.32 mmol, 31.5%). Single crystals were obtained by slow diffusion of hexane into a concentrated solution of the product in THF at room temperature. ^1H NMR (300 MHz, $CDCl_3$, δ): 6.53 (dd, $J = 4.3$, 2.6 Hz, 2H), 6.84 (dd, $J = 4.3$, 3.0 Hz, 2H), 8.11 (d, $J = 12.8$ Hz, 4H), 8.18 (s, 2H); ^{13}C NMR (150 MHz,

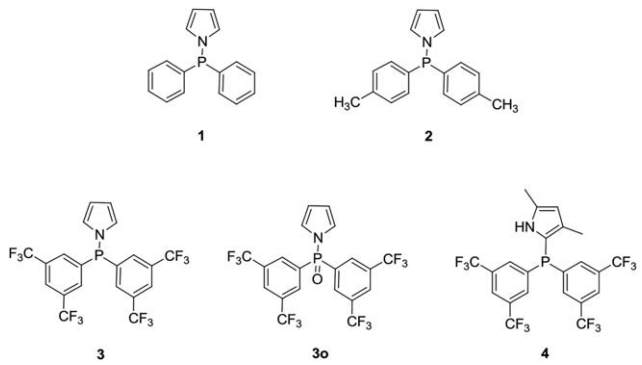

FIGURE 1 Structures of the ligands examined in this study.

$CDCl_3$, δ): 115.48, 122.56 (q, $^1J_{C-F} = 273$ Hz), 123.10, 127.79, 132.13, 132.24 ($^1J_{C-P} = 129$ Hz), 133.28 (qd, $^2J_{C-F} = 34$ Hz and $^3J_{C-P} = 14$ Hz); ^{31}P NMR (242 MHz, $CDCl_3$, δ): 18.04; purity = 98% on the basis of ^{31}P NMR analysis. HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_{20}H_{10}F_{12}NOPNa$, 562.0206; found, 562.0207.

4: Bis(3,5-Bis(Trifluoromethyl)Phenyl)(3,5-Dimethyl-1H-Pyrrol-2-yl)Phosphine

Following the general procedure, 2,4-dimethylpyrrole (0.2 mL, 2 mmol), Et_3N (0.3 mL, 2.2 mmol), bis(3,5-(trifluoromethyl)phenyl)chlorophosphine (0.49 g, 1 mmol), and dichloromethane were used. The product as a red oil was purified by column chromatography on silica gel, with ethyl acetate as the eluent. The solvent was removed under vacuum to give the product as a red oil (0.28 g, 0.49 mmol, 49.0%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 2.15 (s, 3H), 2.24 (s, 3H), 5.95 (s, 1H), 7.42 (s, N—H), 7.69 (d, J = 6.4 Hz, 4H), 7.86 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, δ): 12.47, 13.39, 111.51, 112.57, 122.91, 123.20 (q, $^1J_{C-F} = 273$ Hz), 132.13, 132.37, 134.22, 135.30, 140.42; ^{31}P NMR (242 MHz, $CDCl_3$, δ): −31.98. Purity 91% on the basis of ^{31}P NMR analysis.

Procedure for Ethylene Oligomerization

These reactions were carried out in a 125 mL Parr reactor equipped with a pressure controller. The reactor was charged with methylcyclohexane (47 mL) and the desired amount of Al co-catalysts. After the solution was stirred for 15 min at the set temperature using a thermostat bath, it was saturated with N_2 gas. The catalyst solution of $Cr(acac)_3$ (0.01 mmol) and the ligand (0.02 mmol) was methylcyclohexane (3 mL). Time zero for the reaction was considered the point at which the catalyst solution was injected into the reactor with ethylene gas. After 30 min, the reaction was terminated by discontinuing the ethylene feed and cooling the reactor to below 0 °C in an ice bath. After releasing the excess ethylene from the reactor, nonane (1 mL) was added as an internal standard for GC-FID analysis of the liquid phase. The mixture was quenched with methanol (5 mL). A small amount of reaction solution was collected and analyzed by GC-FID to determine the distribution of oligomers obtained. The remainder of the mixture was quenched with a mixture of methanol (450 mL) and diluted hydrochloric acid (5 mL) to precipitate the solid product, which was isolated by filtration and dried in a vacuum oven at 60 °C. The oligomers were analyzed by GC-FID for oligomer composition.

Computational Details

The DFT calculations were performed using the Orca program (ver. 3.0.3).[18] Geometry optimization was carried out with B97-D3 functional,[19,20] which showed good performance for modeling organometallic complexes,[21] with def2-TZVP(-f) used as the basis set.[22] Single point energies at the optimized geometries were obtained with double-hybrid PWPB95-D3 functional[23] and def2-TZVP as the basis set. Solvation by methylcyclohexane was accounted for using the conductor-like screening model (COSMO)[24] in all calculations. Transition state geometries were initially estimated and then confirmed after optimization to give an imaginary vibrational mode along the reaction coordinate.

RESULTS AND DISCUSSION

The ligands used in this study (Fig. 1) were prepared by reaction of pyrrole with triethylamine and then chlorodiarylphosphine to form each ligand *via* salt elimination followed by column chromatography (Scheme S1).[17,25] Among them, **1** and **2** had an aminophosphine structure with no oxygen (O) bound to the phosphine atom even after purification by column chromatography under ambient conditions; their structures were confirmed by spectroscopic data and X-ray single-crystal analysis of **2** (Fig. 2). In contrast, the same procedure using chlorodiarylphosphine bearing trifluoromethyl groups on the phenyl rings yielded phosphine oxide, **3o**, confirmed by X-ray single-crystal analysis (Fig. 3). It is well known that related phosphine compounds are readily oxidized upon exposure to air, resulting in phosphine oxides.[26–28] To obtain **3**, all synthetic and purification processes were carried out under an N_2 atmosphere. Although attempts to isolate a single crystal of **4** were unsuccessful, the spectroscopic analysis of **4** supported a phosphine structure (see Supporting Information for details).

To elucidate the effects of ligand modification on activity and selectivity, ethylene oligomerization reactions were carried

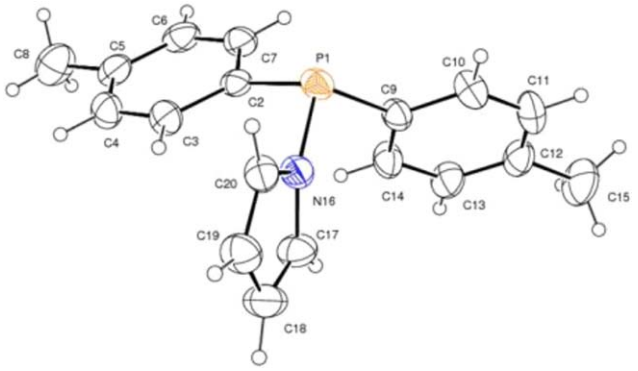

FIGURE 2 Thermal ellipsoid representation (30% probability boundaries) of the X-ray crystal structure of **2**. [Color figure can be viewed at wileyonlinelibrary.com]

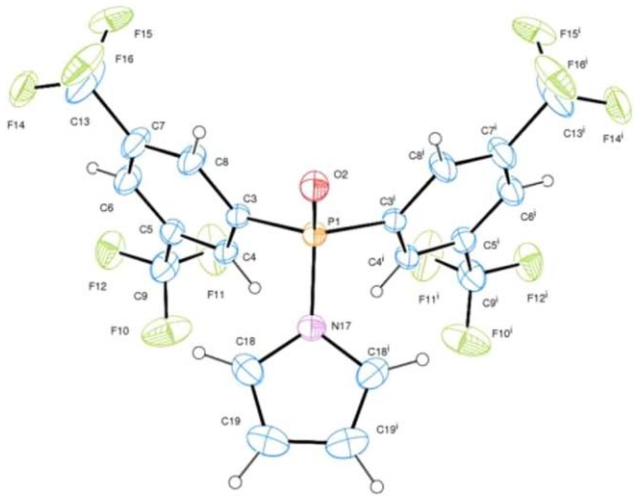

FIGURE 3 Thermal ellipsoid representation (30% probability boundaries) of the X-ray crystal structure of **3o**. [Color figure can be viewed at wileyonlinelibrary.com]

out by using Cr(III) pre-catalysts generated *in situ* by mixing the ancillary ligands with chromium(III) acetylacetonate ($Cr(acac)_3$) and alkyl aluminum co-catalyst. Attempts to obtain further insights into the connectivity in the chromium complexes by isolating single crystals suitable for X-ray diffraction analysis were unsuccessful. The pertinent results regarding the catalytic behavior and properties of the polymers are summarized in Tables 1 and 2.

First, we compared the catalytic behaviors of **1**/$Cr(acac)_3$, **2**/$Cr(acac)_3$, and **3o**/$Cr(acac)_3$ upon activation of dry methylaluminoxane (DMAO) under 10 bar of ethylene (entries 1–3 in Table 1). During this initial screening, the ethylene oligomerization selectivity toward 1-hexene of the catalyst systems containing **2** and **3o** were much lower than that of **1**, affording a large amount of polyethylene (PE) as the major product. The amount of PE was too high to be part of the statistical product distribution, suggesting that a polymerization catalyst co-exists in the catalytic system. Previous reports that highlighted the profound influence of this type of activator on the ethylene oligomerization selectivity prompted us to use different aluminum co-catalysts of various compositions.[29–31] Interestingly, when the above experiments were carried out on activation of a dry methylaluminoxane/triisobutylaluminum (DMAO/TIBA) mixture, a considerable change in the catalytic behavior was observed (entries 4–6); the *in-situ* activation of **1**, **2**, or **3o** with a DMAO (500 eq)/TIBA (50 eq) mixture in the presence of $Cr(acac)_3$ resulted in a large amount of the liquid product, linear alpha-olefins (LAO) with 1-hexene as a major product, whereas the PE formation was highly reduced. In particular, the reaction of **3o**/$Cr(acac)_3$ under this condition produced 96.3 mol % of 1-hexene out of 0.96 g LAO, along with only a trace amount of PE (0.06 g, 6.2 wt %). This promising catalytic performance of **3o**/$Cr(acac)_3$ prompted an investigation into this catalytic system under various reaction conditions, with the aim of further improving the activity and selectivity for 1-hexene formation.

When the influence of the reaction conditions on the catalytic behavior was systematically investigated with **3o**/$Cr(acac)_3$, both the selectivity and catalytic activity were dramatically influenced by the choice of the activator and solvent, as summarized in Table 2. First, under typical ethylene oligomerization conditions, on activation with a toluene solution of MAO (10 wt %), ethylene oligomerization with **3o**/$Cr(acac)_3$ resulted in a nonselective distribution of oligomers including 66 mol % of C_{10}–C_{40} (entry 7). Various examples are reported where the presence of toluene poisons the selective ethylene oligomerization catalyst and results in a nonselective distribution of ethylene oligomers.[32–34] The switch in catalytic behavior may be due to interference of toluene with the catalytically active chromium species *via* coordination, although direct evidence has not been reported.[35] Thus, to avoid using toluene, DMAO was chosen as an activator instead of MAO in toluene. Whereas the use of MAO in toluene resulted in a statistical distribution of oligomers, the switch to the toluene-free system using DMAO and methylcyclohexane as a solvent changed the selectivity from higher oligomers to 1-hexene (67 mol %), although the major product was a significant amount of PE (entry 8). This shift in selectivity indicates that, for the current system, a small amount of toluene plays a crucial role in determining the selectivity for 1-hexene versus higher oligomers.

TABLE 1 Ethylene Oligomerization with **1–3o**/$Cr(acac)_3$

Entry	Ligand	Activator	Al/Cr (equiv)	PE (g)	LAO (g)	PE (wt %)	Activity[a] (g/mmol Cr/h)	1-C_6[b] (mol %)	1-C_8[b] (mol %)	C_{10}-C_{40}[b] (mol %)
1	**1**	DMAO	500	0.059	0.229	20.5	57.6	90.1	3.9	6.0
2	**2**	DMAO	500	0.563	0.065	89.6	125.7	66.4	10.0	23.6
3	**3o**	DMAO	500	0.489	0.050	90.7	107.8	48.7	14.0	37.3
4	**1**	DMAO/TIBA	500/50	0.069	0.337	17.0	81.3	88.3	3.2	1.0
5	**2**	DMAO/TIBA	500/50	0.054	0.321	14.4	74.9	94.7	2.4	1.5
6	**3o**	DMAO/TIBA	500/50	0.063	0.957	6.2	203.9	96.3	0.8	0.5

General conditions: $Cr(acac)_3$ 0.01 mmol, ligand 0.02 mmol, ethylene 10 bar, methylcyclohexane 50 mL, 80 °C, 30 min.

[a] In units of [g of total products (PE + oligomers)]·(mmol Cr)$^{-1}$·h^{-1}.
[b] The % yield as measured by GC-FID.

TABLE 2 Effects of Activator Compositions and Reaction Conditions on Selective Ethylene Oligomerization

Entry	Ligand	Activator	Al/Cr (equiv)	PE (g)	LAO (g)	PE (wt %)	Activity[a] (g/mmol Cr/h)	1-C_6[b] (mol %)	1-C_8[b] (mol %)	C_{10}-C_{40}[b] (mol %)
7	**3o**	MAO	500	0.348	1.536	18.5	376.8	17.3	16.9	65.7
8	**3o**	DMAO	500	0.863	0.234	78.7	219.4	67.1	11.2	21.8
9	**3o**	DMAO/TIBA	500/100	0.103	2.122	4.6	444.9	98.7	0.5	0.8
10	**3o**	DMAO/TIBA	500/250	0.097	5.252	1.8	1069.8	98.9	0.3	0.8
11	**3o**	DMAO/TIBA	250/250	0.036	6.204	0.6[c]	1248.0	98.5	0.2	1.2
12	**1**	DMAO/TIBA	250/250	0.075	0.963	7.2	207.6	85.1	9.1	2.0
13	**2**	DMAO/TIBA	250/250	0.068	0.918	6.9	197.2	93.1	3.6	1.3
14	**3**	DMAO/TIBA	250/250	0.241	1.226	16.4	293.5	96.8	0.9	2.1
15	**4**	DMAO/TIBA	250/250	0.169	0.169	43.6	77.5	85.0	4.9	6.8
16[d]	**3o**	DMAO/TIBA	250/250	0.105	0.964	9.8	213.8	97.8	0.4	0.6
17[e]	**3o**	DMAO/TIBA	250/250	0.111	3.965	2.7	815.1	98.4	0.5	1.2
18[f]	**3o**	DMAO/TIBA	250/250	0.060	1.503	3.8	312.6	98.5	0.6	0.9
19[g]	**3o**	DMAO/TIBA	250/250	0.145	5.299	2.7	1088.7	96.4	0.7	2.8
20	**DMP**	DMAO/TIBA	250/250	0.031	4.223	0.7	850.8	97.5	0.5	2.0

General conditions: $Cr(acac)_3$ 0.01 mmol, ligand 0.02 mmol, ethylene 20 bar, methylcyclohexane 50 mL, 80 °C, 30 min.
[a] In units of [kg of total products (PE + oligomers)]·(mol Cr)$^{-1}$·h^{-1}.
[b] The % yield as measured by GC-FID.
[c] M_w = 1625 g/mol, polydispersity (M_w/M_n) = 31.4.
[d] $CrCl_3(THF)_3$ 0.01 mmol.
[e] 60 °C.
[f] Ligand 0.01 mmol.
[g] Methylcyclohexane 100 mL.

Next, we carried out ethylene oligomerization under various DMAO/TIBA ratios. Both the selectivity and catalytic activity were significantly affected by the composition of the aluminum co-catalysts. As aforementioned, the activation of **3o**/$Cr(acac)_3$ with DMAO as the only activator generated 67 mol % 1-hexene in 0.23 g LAO, along with 0.86 g of PE (entry 8). However, when TIBA was added, a very positive effect on the catalytic activity was observed; **3o**/$Cr(acac)_3$ activated by 500 eq/100 eq of DMAO/TIBA (entry 9) showed a 10-fold increase in the formation of LAO (0.23 g to 2.12 g) and a significant drop in PE (0.86 g to 0.10 g). The selectivity for 1-hexene was also improved by up to 98.7 mol %. An increase in the amount of TIBA up to 250 eq resulted in even higher LAO yields (5.25 g) with 98.9 mol % 1-hexene selectivity (entry 10), implying that the formation of an active species responsible for selective ethylene trimerization was promoted by TIBA. The best activity of the catalyst was achieved when the activator composition of DMAO/TIBA was 250 eq/250 eq, reaching an activity of about 1250 g (mmol of Cr)$^{-1}$ h^{-1} with 98.5 mol % of 1-hexene in the 6.2 g (99.4 wt %) liquid fraction (entry 11). The polymer formation was considerably reduced (0.6 wt %) under this condition. It is important to avoid PE formation, because the unwanted solid byproduct poses serious reactor-fouling problems that complicate industrial applications.

Then, under the reaction conditions used for entry 11, ethylene oligomerization was carried out with the catalyst system containing **1** or **2** to compare the performance between the ligands; the activity achieved with **1** or **2** was considerably lower than that with **3o** (entries 11–13), suggesting that the highest activity achieved with **3o** was due to its phosphine oxide structure or the presence of CF_3 groups. Under the same conditions, ligand **4** promoted ethylene trimerization. However, activity was much lower, and a significant amount of PE formed (44%; entry 15), implying that the presence of CF_3 groups is not likely the only parameter for improving catalytic activity for 1-hexene.

To identify the origin of the high selectivity achieved with **3o**, we prepared **3** under air-free conditions successfully and carried out ethylene oligomerization (entry 14). Interestingly, the results were very similar to those of **1** and **2** in terms of activity and selectivity, indicating that phosphine oxide is critical for improving the activity of the ligand series (Fig. 4). In addition, we carried out ethylene oligomerization using 2,5-dimethylpyrrole (**DMP**) (from the well-known Philips system) under our reaction conditions to compare the

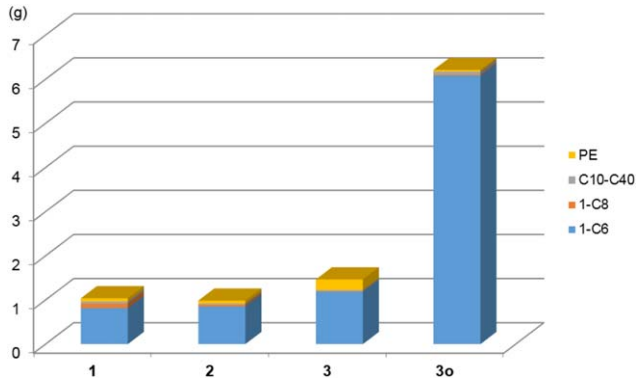

FIGURE 4 Product distribution depending on the ligands (entries 11–14). [Color figure can be viewed at wileyonlinelibrary.com]

performance with that of our ligands (entry 20).[36] Although **DMP** showed excellent selectivity and activity [851 g (mmol of Cr)$^{-1}$ h^{-1} with 97.5 mol % 1-hexene in the 4.2 g liquid fraction], the performance of **3o** is comparable or superior to that of **DMP**, supporting the importance of the $[(CF_3)_2C_6H_3]_2P(O)$ moiety attached to pyrrole.

High-temperature gel permeation chromatography and ^{13}C NMR analyses of the PE produced with **3o**/Cr(acac)$_3$ (entry 11) revealed that the polymer is highly branched and polydisperse (PDI = 31.4, M_n = 1625 g/mol) (Figs. S23 and S25). The formation of the branched products can be attributed to the incorporation of *in-situ*-generated 1-hexene into the polymer chain. This branching is also reflected in the low melting temperature of the polymer (T_m = 123 °C; Fig. S24).

From the results described so far, we found that both the selectivity for 1-hexene and the catalytic activities were dramatically influenced by the choice of the activators and the presence of toluene. The influence of other reaction conditions, including Cr precursor (entry 16), reaction temperature (entry 17), ligand/Cr ratio (entry 18), and the solvent volume (entry 19), were subsequently investigated and compared to the best result obtained for **3o**/Cr(acac)$_3$ (entry 11). Despite the similar selectivity toward 1-hexene, all variations including the use of chromium(III) chloride tetrahydrofuran complex ($CrCl_3(THF)_3$) instead of Cr(acac)$_3$, lower reaction temperature (60 °C), and a lower ligand to Cr ratio were unsuccessful, leading to a reduction in the amount of LAO produced. Similar selectivities for 1-hexene indicate generation of the same active species regardless of the type of Cr precursor and temperature. Changing the ligand/Cr ratio from 2 to 1 also resulted in the decline of activity, indicating a possible change in the coordination environment for the chromium. Doubling the quantity of the reaction solvent did not enhance the performance of the catalyst and had only minor effects on activity and selectivity.

To explore the possible reasons for the differences in the activities of the ligands, we carried out density functional theory (DFT) calculations on one of the main active intermediates in the hypothetical metallacycle mechanism for ethylene trimerization with **2**/Cr and **3o**/Cr catalysts (Fig. S26). A metallacycle mechanism involving the Cr(I)/Cr(III) redox cycle was assumed,[37–40] including coordination of two ethylene molecules to the catalysts with sextet Cr(I), spin-crossing into a quartet, and C—C coupling in the quartet spin state to generate a chromacyclopentane with an oxidation state of Cr(III).[41] The **3o**/Cr exhibited a lower activation barrier for C—C coupling (18.0 kcal/mol above the sextet state; 22.7 kcal/mol for **2**/Cr) and less endothermicity for metallacycle formation (6.3 kcal/mol above the sextet state; 12.0 kcal/mol for **2**/Cr); both of these factors are consistent with a higher activity of **3o**/Cr.

CONCLUSIONS

A series of new ligands **1**–**4** and the corresponding *in-situ*-formed chromium catalysts were evaluated for their selective ethylene oligomerization capabilities. We found that the ligand structure, as well as the type and composition of the activators, had a profound influence on both the selectivity and activity, whereas the reaction temperature, ligand/Cr ratio and solvent volume had only modest effects on the activity. By carefully adjusting the reaction conditions, **3o**/Cr(acac)$_3$ activated by TIBA and DMAO resulted in a highly active PE-free selective ethylene trimerization system, achieving an activity of 1248 g (mmol Cr)$^{-1}$ h^{-1} with 98.5% of 1-hexene, with only a negligible amount of PE (0.6 wt %).

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