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Chromium-Based Complexes Bearing Aminophosphine and Phosphine−Imine−Pyrryl Ligands for Selective Ethylene Tri/Tetramerization

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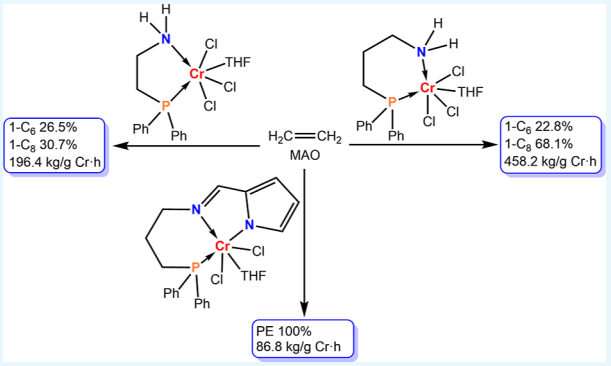
ABSTRACT: A series of Cr-based complexes **6**−**10** bearing aminophosphine (P,N) ligands $Ph_2P-L-NH_2$ [L = CH_2CH_2 (**1**), L = $CH_2CH_2CH_2$ (**2**), and L = $C_6H_4CH_2$ (**3**)] and phosphine−imine−pyrryl (P,N,N) ligands 2-$(Ph_2P-L-N{=}CH)C_4H_3NH$ [L = $CH_2CH_2CH_2$ (**4**) and L = $C_6H_4CH_2$ (**5**)] were prepared, and their catalytic properties were examined for ethylene tri/tetramerization. X-ray crystallographic analysis of complex **8** indicated the κ^2-P,N bidentate coordination mode at the Cr(III) center and the distorted octahedral geometry of monomeric P,N−$CrCl_3$. Upon activation by methylaluminoxane (MAO), complexes **7**−**8** bearing P,N (PC_3N backbone) ligands **2**−**3** showed good catalytic reactivity for ethylene tri/tetramerization. On the other hand, complex **6** bearing the P,N (PC_2N backbone) ligand **1** was found active for non-selective ethylene oligomerization, while complexes **9**−**10** bearing P,N,N ligands **4**−**5** only produced polymerization products. In particular, the high catalytic activity of 458.2 kg/(g·Cr·h), excellent selectivity of 90.9% (1-hexene and 1-octene combined), and extremely low PE content of 0.1% were obtained with complex **7** in toluene at 45 °C and 45 bar. These results suggest that rational control of P,N and P,N,N ligand backbones, including a carbon spacer and rigidity of a carbon bridge, can lead to the high-performance catalyst for the ethylene tri/tetramerization process.



1. INTRODUCTION

Linear α-olefins (LAOs) are key intermediates for the production of commodity polymers (1-C_4 to 1-C_8), poly-alpha-olefins (1-C_8 to 1-C_{14}), plasticizer alcohols (1-C_6 to 1-C_{10}), detergent alcohols (1-C_{12} to 1-C_{14}), and lubricant additives (1-C_{10+}). By the end of 2020, the global production of LAOs has exceeded 5 million metric tons, in which the capacities of 1-hexene and 1-octene have reached 1 000 000 and 800 000 metric tons, respectively.[1] 1-Hexene and 1-octene are widely used as co-monomers for high-quality polyolefin production.[2−5] The growing need for polyolefin products has resulted in the strong demand for 1-hexene and 1-octene. Moreover, the physical and mechanical properties of polyethylene products can be effectively improved by introducing 1-hexene and 1-octene monomers into a polyethylene chain backbone.[6,7] Currently, 1-hexene and 1-octene are mainly produced by ethylene oligomerization. In general, the non-selective ethylene oligomerization method mostly produces the oligomers with Schulz−Flory distribution, which require intensive energy to further separate the individual component from the mixture.[8−10] However, the ethylene tri/tetramerization method, which directly and selectively produces 1-hexene and 1-octene, has attracted considerable research interests from both academic and industrial communities.[11,12]

The first selective ethylene tri/tetramerization system with Cr-based catalysts containing bis(diphenylphosphino)-amine (PNP), bis(diphenylphosphino) hydrazine (PNNP), or 1,2-bis(diphenylphosphino)ethane (dppe) ligand was discovered by Sasol in 2004.[13,14] A selectivity of 68.3% for 1-octene was obtained at 45 bar and 45 °C, along with the remaining products, which include 1-hexene, C_6 impurities, oligomers with higher carbon number, and polyethylene. Subsequently, in order to further improve the ethylene tri/tetramerization performance, typical PCCP,[15−20] PCN,[21] PC_2NCN,[22] PCNP,[23] PCSiNP,[24] PNCN,[25,26] PNCNP,[27] and PNPN[28,29] backbone ligands have been studied. Results show that multidentate ligands containing P and N donors have great potential to catalyze the selective ethylene oligomerization, yielding 1-hexene and 1-octene with high selectivities.[30,31] In a previous work, Yang and co-workers introduced the pyridine−phosphine (PNCN) ligand variations by modifying the

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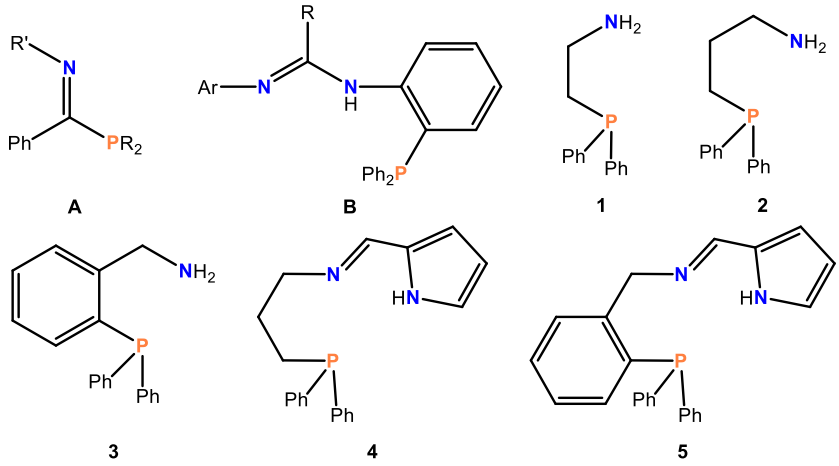
Chart 1. Selected P,N (PCN backbone) ligand A[21], P,N,N (PC_2NCN backbone) ligand B[22], and targeted P, N and P,N,N ligands 1−5.



phosphine substituents, which affected the ligand bite angles and flexibility.[32] These results suggest that a minor modification in the ligand structure can produce remarkable effects on catalytic performance toward α-olefins or polyethylene and oligomeric product distribution. Radcliffe's group investigated Cr-based catalysts bearing 1-phosphanyl methanimine (PCN) ligands (Chart 1A) for selective ethylene tri/tetramerization, and they reported up to 95% selectivity of liquid fraction (1-hexene and 1-octene). After the modification by phosphine substituents or imine substituents of PCN, the pure trimerization selectivity can be transformed into the mixed tri/tetramerization with a 1-octene/1-hexene ratio of 1.7/1.[21] In our previous work, phenyl-linked amidinato-phosphino (PC_2NCN) ligands (Chart 1B) were synthesized for Cr-catalyzed ethylene tri/tetramerization. The results showed that with the modification of imine substituents or carbon-bridged substituents of the PC_2NCN backbone, the 1-octene/1-hexene ratio varied from 0.8 to 1.6.[22] These results indicated that the modification of phosphine substituents, imine substituents, or carbon-bridged substituents of P,N ligands can affect the catalytic selectivity and activity for ethylene tri/tetramerization. However, the detailed carbon bridge backbone structure of P,N and P,N,N ligands, in particular their effects on Cr-catalyzed ethylene tri/tetramerization, has not been studied in depth.

In this paper, we report a series of Cr-based catalysts of complexes **6**−**10** bearing P,N ligands **1**−**3** and P,N,N ligands **4**−**5** (Chart 1, **1**−**5**) for selective ethylene tri/tetramerization. Ligands **1**−**5**, with different carbon spacers and rigidity of carbon bridge, were used to study the effect of ligand backbone structures on catalytic ethylene tri/tetramerization. With MAO co-catalyst, complexes **7**−**8** bearing P,N (PC_3N backbone) ligands **2**−**3** were found active and selective for 1-hexene and 1-octene production, while complexes **9**−**10** bearing P,N,N ligands **4**−**5** were good catalysts for ethylene polymerization. The formation mechanism of polyethylene with high molecular weight was investigated by solid-state ^{13}C nuclear magnetic resonance (NMR) analysis. Furthermore, ethylene pressure, reaction temperature, Al/Cr molar ratio, chromium source, and solvent type were optimized with a complex 7/MAO system to achieve the best catalytic performance of ethylene tri/tetramerization.

2. EXPERIMENTAL SECTION

2.1. Materials and Instrument. All reagents were purchased from commercial sources without further purification before use, unless otherwise stated. Polymeric-grade ethylene and high-purity argon (99.999%) and nitrogen (99.999%) gases were obtained from Jiangsu Hongren Special Gas Co., Ltd. Co-catalyst MAO (10% solution in toluene) was purchased from AkzoNobel company. $CDCl_3$ was degassed and dried over CaH_2. P,N ligands **1**−**3** [$Ph_2PCH_2CH_2NH_2$ (1), $Ph_2PCH_2CH_2CH_2NH_2$ (2), and 2-$Ph_2PC_6H_4CH_2NH_2$ (3)] were synthesized according to the procedures reported in the literature.[33,34] $CrCl_3(THF)_3$ was prepared according to the literature.[35] The Schlenk technique or the MBRAUN glove box under Ar gas condition was employed to treat humidity- and oxygen-sensitive compounds. The used *n*-hexane, tetrahydrofuran, and toluene solvents were dried and refluxed successively under N_2 gas condition.

Crystallographic data were recorded on an Xcalibur, Sapphire 3, Gemini ultra. The ^1H NMR, $^{13}C\{^1H\}$ NMR, and $^{31}P\{^1H\}$ NMR spectra of ligands **1**−**5** were recorded on a Bruker 400 MHz or a 500 MHz spectrometers (Figures S1−S15). Elemental analysis results were obtained on a Thermo Quest Italia SPA EA 1110 instrument. The collected liquid products were identified and analyzed on a Shimadzu GC-2014C instrument with a flame ionization detector (FID) detector and an Inc19091Z-236 HP-1 capillary column (60 m × 0.25 mm).

2.2. Preparation of P,N Ligands 4−5. *2.2.1. 2-($Ph_2PCH_2CH_2CH_2N{=}CH)C_4H_3NH$ Ligand 4.* The as-obtained $Ph_2PCH_2CH_2CH_2NH_2$ ligand **2** (1.20 g, 5.0 mmol) was added into a suspension of pyrrole-2-carboxaldehyde (1.30 g, 5.0 mmol) and anhydrous $MgSO_4$ (in excess) in tetrahydrofuran (THF) (50 mL). The mixture was treated by mechanically stirring for 24 h at room temperature. The residual THF solvent was fully filtered and removed under reduced pressure. After that, the product was collected and rinsed with *n*-hexane (5 mL), obtaining the off-white solid as ligand **4** (1.48 g, 92%). ^1H NMR (500 MHz, $CDCl_3$, 298 K, ppm): δ = 1.82 (m, 2 H, CH_2), 2.12 (m, 1 H, CH_2), 3.64 (t, J = 6.7 Hz, 1 H, CH_2), 6.26 (m, 1 H), 6.50 (dd, 1 H, J = 3.5, 1.1 Hz), 6.88 (s, 1 H) (pyr−*H*), 7.34 (d, J = 3.6 Hz, 6 H), 7.44 (td, J = 7.3, 3.1 Hz, 4 H) (C_6H_5), 8.07 (s, 1 H, N=C*H*), 9.89 (br, 1 H, pyr−N*H*). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 298 K, ppm): δ = 25.64 (d,

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ACS Omega 2023, 8, 18290−18298

J = 11.8 Hz, CH_2), 27.74 (d, J = 16.4 Hz, CH_2), 61.51 (d, J = 13.1 Hz, CH_2), 109.73 (s), 114.64 (s), 122.26 (s), 128.54 (m), 130.23 (s), 132.83 (d, J = 18.3 Hz), 138.82 (d, J = 12.9 Hz), 152.63 (s) (pyr−C and C_6H_5), 179.63 (s, N═CH). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 298 K, ppm): δ = −16.45 (PPh_2). Anal. Calcd for $C_{20}H_{21}N_2P$ (M_r = 320.38): C, 74.98; H, 6.61; N, 8.74. Found: C, 75.03; H, 6.57; N, 8.79.

2.2.2. 2-(2-$Ph_2PC_6H_4CH_2N$═CH)C_4H_3NH Ligand 5. Ligand **5** was synthesized with a similar process of ligand **4**, except for replacing the starting material of ligand **2** by ligand **3** (2.40 g, 5.0 mmol). After being filtered and rinsed, the white solid product was collected as ligand **5** (1.66 g, 90%). ^1H NMR (500 MHz, C_6D_6, 298 K, ppm): δ = 5.01 (s, 2 H, NCH_2), 6.15 (dd, J = 3.4, 2.7 Hz, 1 H, pyr−H), 6.30 (m, 2 H, pyr−H), 6.97−7.44 (m, 14 H, C_6H_4 and C_6H_5), 7.62 (s, 1 H, N═CH), 9.16 (br, 1 H, pyr−NH). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 298 K, ppm): δ = 62.44 (d, J = 22.1 Hz, CH_2), 109.41 (s, pyr−C), 114.60 (s), 122.03 (s), 127.16 (s), 128.52 (m), 129.00 (s), 130.18 (s), 134.04 (s), 135.58 (d, J = 15.0 Hz), 137.29 (d, J = 10.9 Hz), 144.72 (d, J = 24.4 Hz) (pyr−C, C_6H_4 and C_6H_5), 152.54 (s, N═CH). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 298 K, ppm): δ = −15.67 (PPh_2). Anal. Calcd for $C_{24}H_{21}N_2P$ (M_r = 368.42): C, 78.24; H, 5.75; N, 7.60. Found: C, 78.32; H, 5.79; N, 7.68.

2.3. Preparation of Cr-Based Complexes 6−10.

2.3.1. $Ph_2PCH_2CH_2NH_2CrCl_3$(THF) Complex 6. The solution of ligand **1** (0.23 g, 1.0 mmol) in THF (15 mL) was added dropwise into the $CrCl_3(THF)_3$ (0.37 g, 1.0 mmol) suspension in THF (15 mL) at room temperature. After being stirred constantly for 12 h, the solution color changed from purple-red to blue-green. The THF solvent was evaporated under reduced pressure. The residue was collected and fully rinsed with *n*-hexane (5 mL), producing the blue-green solid product as complex **6** (0.42 g, 91%). Anal. Calcd for $C_{18}H_{24}Cl_3CrNOP$ (M_r = 459.72): C, 47.03; H, 5.26; N, 3.05. Found: C, 46.96; H, 5.17; N, 3.11.

2.3.2. $Ph_2PCH_2CH_2CH_2NH_2CrCl_3$(THF) Complex 7. Complex **7** was synthesized with a similar process of complex **6**, except for replacing the starting material of ligand **1** by ligand **2** (0.24 g, 1.0 mmol). After being filtered and rinsed, the blue-green solid product was collected as complex **7** (0.44 g, 93%). Anal. Calcd for $C_{19}H_{26}Cl_3CrNOP$ (M_r = 473.74): C, 48.17; H, 5.53; N, 2.96. Found: C, 48.25; H, 5.49; N, 2.87.

2.3.3. 2-$Ph_2PC_6H_4CH_2NH_2CrCl_3$(THF) Complex 8. Complex **8** was synthesized with a similar process of complex **6**, except for replacing the starting material of ligand **1** by ligand **3** (0.29 g, 1.0 mmol). After being filtered and rinsed, the blue-green solid product was obtained as complex **8** (0.48 g, 92%). Anal. Calcd for $C_{23}H_{26}Cl_3CrNOP$ (M_r = 521.79): C, 52.94; H, 5.02; N, 2.68. Found: C, 53.03; H, 5.09; N, 2.76.

2.3.4. [2-($Ph_2PCH_2CH_2CH_2N$═CH)C_4H_3N]$CrCl_2$(THF) Complex 9. The solution of *n*BuLi (1.0 mmol) was added dropwise into the suspension of ligand **4** (0.32 g, 1.0 mmol) in THF (35 mL) at −50 °C. Then, the obtained mixture was warmed to −20 °C within 1 h and constantly stirred for another 0.5 h. The solution mixture was cooled to −50 °C again and added dropwise into the suspension of $CrCl_3(THF)_3$ (0.37 g, 1.0 mmol) in THF (15 mL). The mixture was warmed gently to room temperature and then constantly stirred overnight. After the reaction finished, all volatiles were evaporated and removed under reduced pressure. The residue was fully extracted with toluene (25 mL), yielding the green solid product as complex **9** (0.46 g, 89%). Anal. Calcd for $C_{24}H_{28}CrCl_2N_2OP$ (M_r = 514.37): C, 56.04; H, 5.49; N, 5.45. Found: C, 56.13; H, 5.42; N, 5.52.

2.3.5. [2-(2-$Ph_2PC_6H_4CH_2N$═CH)C_4H_3N]$CrCl_2$(THF) Complex 10. Complex **10** was synthesized with a similar process of complex **9**, except for replacing the starting material of ligand **4** by ligand **5** (0.37 g, 1.0 mmol). After being filtered and rinsed, the green solid product was collected as complex **10** (0.51 g, 91%). Anal. Calcd for $C_{28}H_{28}Cl_2CrN_2OP$ (M_r = 562.41): C, 59.80; H, 5.02; N, 4.98. Found: C, 59.86; H, 5.08; N, 5.06.

2.4. X-ray Crystallography Test. Complex 8 was used as a representative sample to generate single-crystal diffraction data. The oil drop method was employed to assemble the crystal sample on the glass fiber. Crystal data was recorded on a single-crystal diffractometer equipped with the graphite monochromatic Mo-Kα radiation source (λ = 0.71073 Å) and a CCD detector. The absorption correction was performed through the spherical harmonics program. In addition, crystal structural analysis was carried out using either the direct method (SHELXS 97) or the intrinsic phasing method (ShelXT).[36] All non-hydrogen atoms of target complex were anisotropically refined. The crystal data and structure refinement of complex 8·THF are listed in Table S1. Relevant crystal data were stored in the Cambridge Crystallographic Data Centre with the publication no. CCDC 2194126.

2.5. Ethylene Oligomerization or Polymerization Reaction. Ethylene oligomerization and polymerization experiments were carried out in a 1.0 L stainless steel autoclave. Prior to use, the autoclave was heated to 80 °C for 4 h in vacuo to ensure the water- and oxygen-free environment. After nitrogen purging three times, the autoclave was cooled naturally to room temperature. Before successively adding the solvents, co-catalyst, and catalyst sample (dissolved in solvent), the autoclave was preheated to a desired temperature. Ethylene gas was continuously fed into the autoclave to ensure the stable temperature and pressure. After the reaction, the ethylene feed was stopped. Meanwhile, the H_2O/glycol cycling system quickly cooled down the reactor to ca. 10 °C. The gas product mixture was collected using gasbags, while the liquid products were quenched with 10% HCl/H_2O solution. The solid products were dried overnight at 60 °C to the constant weight. The solid products were dried overnight at 60 °C to the constant weight. The as-obtained oligomerization products were measured by a gas chromatograph with an FID detector, and results are displayed in Figures S16, S17, with residence times in Tables S2 and S3.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization. P,N bidentate ligands **1**−**3** [$Ph_2PCH_2CH_2NH_2$ (**1**), $Ph_2PCH_2CH_2CH_2NH_2$ (**2**), and 2-$Ph_2PC_6H_4CH_2NH_2$ (**3**)] and P,N,N tridentate ligands **4**−**5** [2-($Ph_2PCH_2CH_2CH_2N$═CH)C_4H_3NH (**4**) and 2-(2-$Ph_2PC_6H_4CH_2N$═CH)C_4H_3NH (**5**)] were prepared in high yield (65−92%). Ligands **2** and **3** were subjected to a one-step dehydration reaction with pyrrole-2-formaldehyde, respectively. The resulting white powders were categorized as ligands **4** and **5**. The prepared ligands **4** and **5** were used to investigate the effect of adding a third ligand-donor group (pyrryl) into the phosphine imine backbone on the catalytic ethylene tri/tetramerization reaction.

In order to verify the successful preparation of P,N,N ligands **4**−**5**, the NMR (^1H, ^{13}C, and ^{31}P) spectrum and CHN elemental analysis were carried out. The ^1H NMR spectra of NH showed the resonances at δ 9.89 ppm for ligand **4** and at δ

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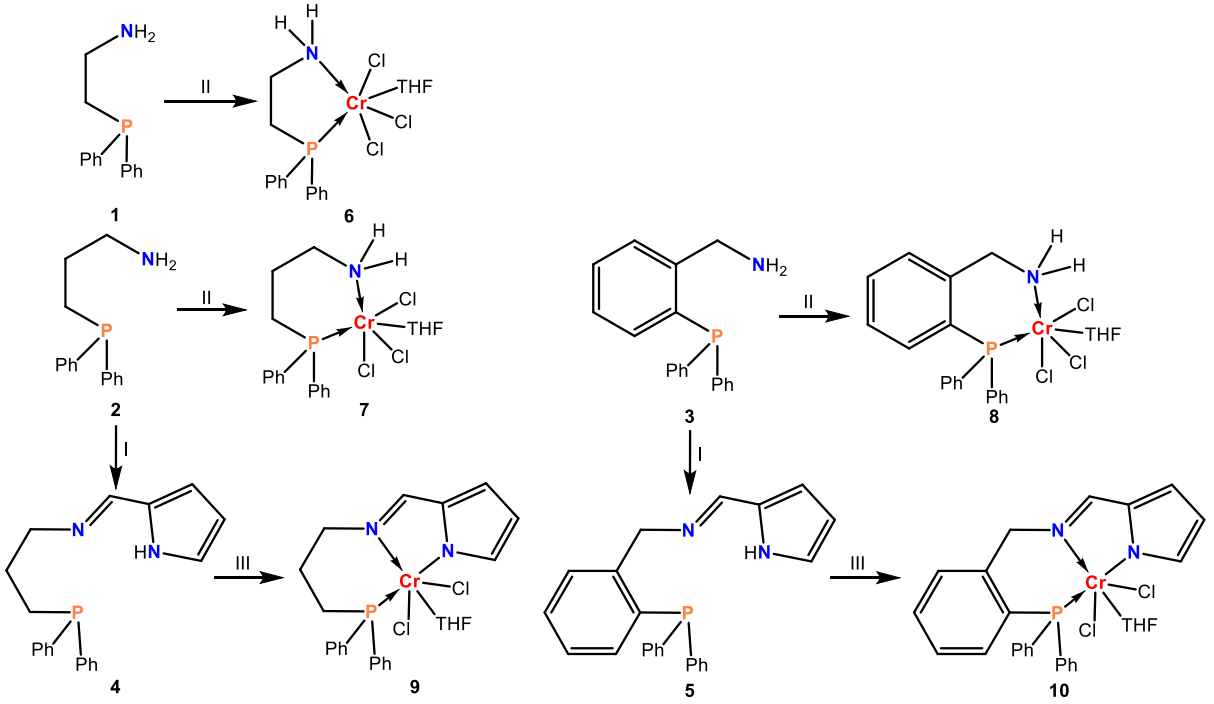
ACS Omega 2023, 8, 18290−18298

Scheme 1. Synthesis of P,N,N Ligands 4−5 and Complexes 6−10[a]



[a]Reagents and conditions: (I) 2-(CHO)C_4H_3NH, $MgSO_4$, THF, RT; (II) $CrCl_3(THF)_3$, THF, RT; and (III) *n*BuLi, $CrCl_3(THF)_3$, THF, −50 → −20 → −50 °C → RT.

9.16 ppm for ligand **5**, which were far away from those of ligands **1**−**3** (δ 1.44 ppm for ligand **1**, δ 1.24 ppm for ligand **2**, and δ 1.55 ppm for ligand **3**).[37] Moreover, the $^{31}P\{^1H\}$ NMR spectra showed the characteristic resonances of the PPh_2 group at δ −16.45 ppm for ligand **4** and at δ −15.67 ppm for ligand **5**. The resonance of the PPh_2 group in ligand **1** was significantly shifted negatively in comparison with those in ligands **2**−**5**, which could be ascribed to the formation of the PC_2N backbone in ligand **1**, instead of the PC_3N backbone in ligands **2**−**5**.

After that, complexes **6**−**10** were further synthesized based on the as-obtained ligands **1**−**5** for the study of catalytic ethylene tri/tetramerization. $CrCl_3(THF)_3$ salt was treated with P,N bidentate ligands **1**−**3** in THF solvent. After removing the residual THF, blue-green solids with high yield (91−93%) were collected as complexes **6**−**8**. Unlike P,N bidentate ligands **1**−**3**, P,N,N tridentate ligands **4** and **5** were pretreated with *n*BuLi in THF at −50 °C ∼ −20 °C, producing the corresponding lithium salts. These lithium salts further directly reacted with $CrCl_3(THF)_3$ at −50 °C ∼ RT, forming the green solids as complexes **9** and **10**. The prepared processes of ligands **4**−**5** and complexes **6**−**10** are displayed in Scheme 1.

The X-ray quality single crystal of complex **8**·THF was obtained by recrystallization in THF/*n*-hexane (3:1, v/v) solution at −20 °C for 48 h. The molecular structure of complex **8**·THF showed monomeric P,N−$CrCl_3$ with a distorted octahedral geometry at the Cr(III) center. As shown in Figure 1, the coordination sphere was made up of one P,N ligand, three Cl atoms, and one THF molecule. Table 1 displays the N(1)−Cr(1)−P(1) angle of 89.06(6)° in complex **8**, which was similar to the reported P−Cr−N angle of 90.96(5)° in Cr-based complexes bearing the P,N,N (PC_3NC_2N backbone) ligand.[38] Similarly, the Cr−P bond

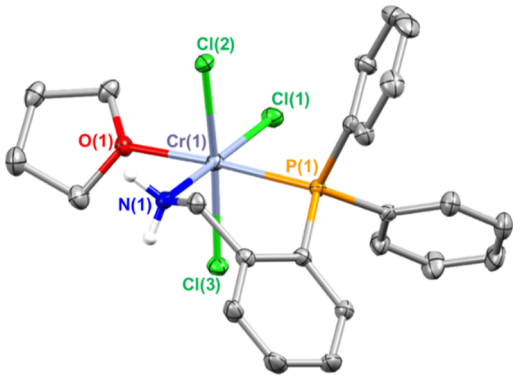


Figure 1. X-ray molecular structure of complex **8**·THF with thermal ellipsoids at 50% probability level. H atoms are omitted for clarity.

Table 1. Selected Representative Bond Lengths (Å) and Angles (°) for Complex 8

complex 8	selected bond lengths (Å) and angles (°)
Cr(1)−P(1)	2.4629(8)
Cr(1)−N(1)	2.085(2)
Cr(1)−Cl(1)	2.3011(8)
Cr(1)−Cl(2)	2.3318(8)
Cr(1)−Cl(3)	2.3043(8)
Cr(1)−O(1)	2.0779(17)
N(1)−C(1)	1.490(3)
N(1)−Cr(1)−P(1)	89.06(6)

distance of 2.4629(8) Å and the Cr−N bond distance of 2.085(2) Å for complex **8** were similar to those found in P,N−Cr or P,N,N−Cr complexes (Cr−P 2.4371−2.772 Å and Cr−N 2.045−2.160 Å).[22,39] The sum of these bond angles (N(1)−Cr(1)−P(1) for 89.06(6)°, P(1)1−Cr(1)−Cl(1) for

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Table 2. Catalytic Results for Ethylene Oligomerization with Complexes 6−10[a]

		oligomer distribution (wt %)[b]								
entry (Cat.)	activity kg/(g·Cr·h)	1-C_4	C_6(1-C_6)	C_8(1-C_8)	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	PE[c] (wt %)
1 (**6**)	196.4	12.2	26.5(100)	30.7(100)	10.3	9.6	6.8	2.4	1.5	4.9
2 (**7**)	215.6	0	29.8(94.1)	59.2(100)	2.4	4.2	3.7	0.4	0.3	0.8
3 (**8**)	226.3	0	35.2(94.0)	52.4(100)	2.9	4.9	3.7	0.4	0.5	1.2
4 (**9**)	86.8	0	0	0	0	0	0	0	0	100
5 (**10**)	98.5	0	0	0	0	0	0	0	0	100

[a]Test conditions: 1.0 L reactor, 180 mL toluene, 10.0 μmol of the catalyst, 700 equiv of MAO, 50 °C, 30 bar, and run time: 47 min. [b]Weight percentage of liquid fraction. [c]Weight percentage of total products.

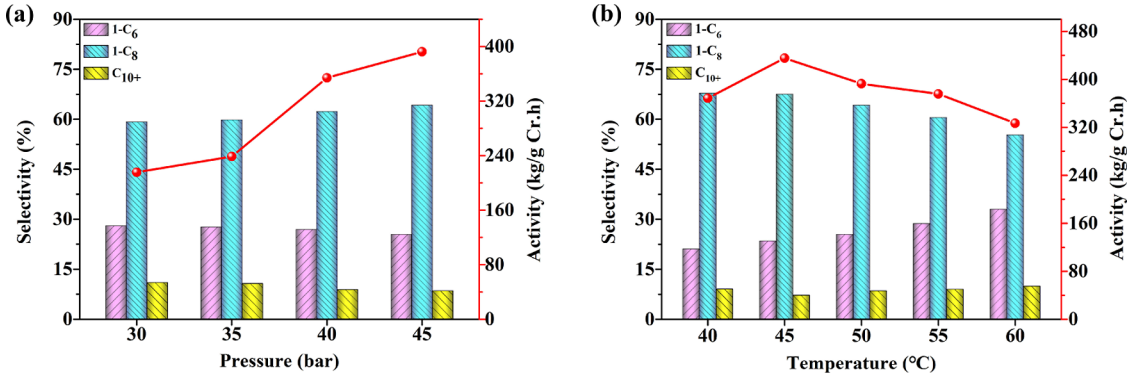

Figure 2. Effects of pressures (a) and temperatures (b) on 1-C_6, 1-C_8, and C_{10+} olefin catalytic performance using the complex 7/MAO system in toluene. General conditions: 1.0 L reactor, 10.0 μmol of the catalyst, Al:Cr = 700, 180 mL of toluene, and run time: 47 min.

89.78(3)°, Cl(1)−Cr(1)−O(1) for 95.26(6)°, and O(1)−Cr(1)−N(1) for 85.93(8)°) around the Cr(1) center in this equatorial plane is 360.03°, indicating the coplanar structure for atoms of N(1), P(1), Cl(1), O(1), and Cr(1). Furthermore, the molecular structure of complex **8**·THF also showed the κ^2-P,N bidentate coordination mode of ligand **3** at the Cr(III) center.

3.2. Effects of Ligand Backbone Structures on Ethylene Tri/tetramerization. Complexes **6**−**10** bearing carbon-bridged P,N bidentate ligands **1**−**3** and P,N,N tridentate ligands **4**−**5** were prepared for catalytic ethylene tri/tetramerization. Prior to reaction, these complexes were activated with 700 equiv of MAO in toluene at 50 °C and 30 bar. The reaction results are summarized in Table 2 (entries 1−5). Complexes **6**−**8** bearing P,N bidentate ligands **1**−**3** were active for ethylene oligomerization reaction, while complexes **9**−**10** bearing P,N,N tridentate ligands **4**−**5** only produced polyethylene products. The significant difference is mainly attributed to the different chelating modes of P,N or P,N,N at the Cr(III) center. The electron and steric hindrance effects of a third ligand-donor group (pyrryl) (**4**−**5**) lead to an obvious change in the coordination environment of the Cr(III) center, compared to the P,N bidentate ligands (**2**−**3**). Similar results have been reported, where chromium complexes with P,N-chelation enabled catalytic ethylene tri/tetramerization, while those with P,N,N-chelation were only active for ethylene polymerization.[40] The catalytic ethylene oligomerization activities of 196.4 kg/(g·Cr·h) for complex **6**, 215.6 kg/(g·Cr·h) for complex **7**, and 226.3 kg/(g·Cr·h) for complex **8** were obtained, while ethylene polymerization activities of 86.8 kg/(g·Cr·h) for complex **9** and 98.5 kg/(g·Cr·h) for complex **10** were obtained, as well. The low catalytic activities toward ethylene polymerization were primarily related to polyethylene accumulated in the polymerization side reaction, which resulted in the gradual deactivation of catalytic active species.[41,42] In order to understand the formation process of polyethylene with high molecular weight, the solid-state ^{13}C NMR spectrum of polyethylene catalyzed by complex **10** was recorded. As shown in Figure S18, only a singlet ^{13}C peak (δ = 32.25) was observed in the chemical shift range of −160 to 335 ppm. These results suggest that polyethylene was more preferred via ethylene homo-polymerization rather than ethylene co-polymerization with 1-hexene or 1-octene.

Interestingly, all of the complexes **6**−**8** bearing two- and three-carbon spacer P,N ligands **1**−**3** were active in ethylene oligomerization, along with a relationship between the carbon spacer structure of the ligand and product selectivity. Specifically, complex **6** bearing the two-carbon spacer ligand **1** presented the non-selective ethylene oligomerization behavior, while both complexes **7** and **8** bearing three-carbon spacer ligands **2** and **3** exhibited the selective catalytic ethylene tri/tetramerization performance. Obviously, the catalytic selectivity of complex **6** was significantly different from that of complex **7**, which could be related to the bite angle of P−Cr−N created by different carbon spacers. For complex **6** or **7**, the Cr center was coordinated with ligand **1** or **2** to form the PC_2N−Cr five-membered ring or the PC_3N−Cr six-membered ring, where the P−Cr−N bite angle of the six-membered ring is larger than that of the five-membered ring. Similar results were reported by other works, where the P−Cr−N bite angles of the NCNP−Cr five-membered ring and the NC_2NP−Cr six-membered ring were 75.84(35) and 92.15(16)°, respectively.[32] Furthermore, 59.2% C_8 selectivity and 29.8% C_6 selectivity were obtained from complex **7** in catalytic ethylene tri/tetramerization. Among all C_6 products, 1-hexene was the major component of 94.1%, and the remaining 5.9% contained primarily methylcyclopentane and methylenecyclopentane in a ratio of 1:1. However, the non-selective oligomerization

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ACS Omega 2023, 8, 18290−18298

Table 3. Reaction Results for Catalytic Ethylene Oligomerization with Complex 7[a]

					oligomer distribution (wt %)[b]			
entry (Cat.)	P (bar)	T (°C)	Cocat. (Al:Cr)	activity kg/(g·Cr·h)	C_6(1-C_6)	C_8(1-C_8)	C_{10+}	PE[c] (wt %)
1 (7)	30	50	MAO (700)	215.6	29.8(94.1)	59.2(100)	11.0	0.8
2 (7)	35	50	MAO (700)	238.7	29.5(93.8)	59.8(100)	10.7	0.9
3 (7)	40	50	MAO (700)	354.2	28.8(93.5)	62.3(100)	8.9	0.8
4 (7)	45	50	MAO (700)	392.5	27.3(93.2)	64.2(100)	8.5	0.5
5 (7)	45	40	MAO (700)	368.6	23.1(91.3)	67.8(100)	9.1	0.3
6 (7)	45	45	MAO (700)	435.2	25.3(92.8)	67.5(100)	7.2	0.2
7 (7)	45	55	MAO (700)	375.6	30.5(94.1)	60.5(100)	9.0	1.1
8 (7)	45	60	MAO (700)	326.8	34.8(94.8)	55.3(100)	9.9	1.0
9 (7)	45	45	MAO (800)	418.5	25.8(93.5)	66.7(100)	7.5	0.8
10 (7)	45	45	MAO (600)	458.2	24.5(93.2)	68.1(100)	7.4	0.1
11 (7)	45	45	MAO (500)	225.8	24.0(93.4)	68.7(100)	7.3	2.6
12[d]	45	45	MAO (600)	186.5	22.9(92.3)	65.2(100)	11.9	2.3
13[e]	45	45	MAO (600)	147.3	23.7(91.8)	63.8(100)	12.5	3.6
14 (7)[f]	45	45	MAO (600)	269.5	24.9(92.3)	67.2(100)	7.9	0.9
15 (7)[g]	45	45	MAO (600)	175.9	23.8(93.1)	67.8(100)	8.4	1.2

[a]General conditions: 1.0 L reactor, 10.0 μmol of the catalyst, 180 mL of toluene, and run time: 47 min. [b]Weight percentage of the liquid fraction. [c]Weight percentage of the total products. [d]12.0 μmol of ligand **2** and 10.0 μmol of $Cr(acac)_3$. [e]12.0 μmol of ligand **2** and 10.0 μmol of $CrCl_3(THF)_3$. [f]Solvent: cyclohexane. [g]Solvent: ethylbenzene.

product distribution of complex **6** effectively ruled out the metalacyclic mechanism.[43] Similarly, the catalytic tri/tetramerization activity of complex **8** with a rigid phenyl backbone ligand was slightly higher than that of complex **7** with an alkyl-substituted backbone ligand, which was probably due to the higher rigidity ligand structure. However, complex **8** was less selective with 52.4% C_8 selectivity and 35.2% C_6 (94.0% 1-C_6) selectivity, which were lower than those of complex **7** with an alkyl-substituted backbone ligand.

3.3. Effects of Reaction Parameters on Ethylene Tri/tetramerization. Complex **7** bearing P,N ligand **2** has delivered the higher C_8 selectivity and less polyethylene formation than complex **8**; hence, complex **7** was selected to study the effects of reaction parameters on catalytic performance. Reaction parameters including ethylene pressure, reaction temperature, Al/Cr molar ratio, chromium source, and solvent type were systemically optimized. First, ethylene pressures (30, 35, 40, and 45 bar) were evaluated with the complex 7/MAO system at 50 °C. As shown in Figure 2a, with the increase of ethylene pressure from 30 to 45 bar, the activity increased from 215.6 kg/(g·Cr·h) to 392.5 kg/(g·Cr·h) (Table 3, entries 1−4), which can be explained by the higher ethylene solubility in toluene under higher pressure. Meanwhile, the C_6 selectivity decreased from 29.8 to 27.3% and the 1-C_6 selectivity in C_6 remained nearly constant from 94.1 to 93.2%, while the 1-C_8 selectivity gradually increased from 59.2 to 64.2% (Table 3, entries 1−4). At 45 bar, the 392.5 kg/(g·Cr·h) catalytic activity, 64.2% C_8 selectivity, and 0.5% PE content were obtained. Based on these results, it can be concluded that high ethylene pressure can facilitate ethylene insertion into metallacycloheptane, which leads to the formation of a metallacyclononane reaction intermediate.[44]

Next, the effects of reaction temperatures (40, 45, 50, 55, and 60 °C) with a complex 7/MAO system at 45 bar were further investigated. As shown in Figure 2b, the catalytic activity of the complex 7/MAO system exhibited volcano shape, and the highest catalytic activity of 435.2 kg/(g·Cr·h) and the lowest PE content of 0.2% were obtained at 45 °C. It is known that the higher reaction temperature can cause the partial deactivation or decomposition of the catalyst. On the other hand, the lower ethylene solubility in toluene at higher temperature can also result in the poor catalytic activity.[26,45] Furthermore, when the reaction temperatures increased, the C_6 selectivity increased from 23.1 to 34.8% and the 1-C_6 selectivity in C_6 from 91.3 to 94.8%, while the 1-C_8 selectivity decreased from 67.8 to 55.3% (Table 3, entries 4−8). These results were consistent with the observation of Blann et al., who reported the temperature impact on the selectivity of 1-C_6 and 1-C_8 for PCNP/Cr tetramerization systems.[46] Coupling with the probable reaction mechanism, it is believed that the stability of the formed metallacycloheptane intermediate was poor at high temperature, and β-hydride transfer and reductive elimination of metallacycloheptane were more favored than further ethylene insertion.[47]

Then, the Al/Cr molar ratios (500, 600, 700, and 800) were optimized for the complex 7/MAO system at 45 °C and 45 bar, as shown in Figure 3. A trend of catalytic activity first increasing and then decreasing was observed. The highest catalytic activity of 458.2 kg/(g·Cr·h) was obtained, along with the extremely low PE content (0.1%), when the molar ratio of Al/Cr was 600. With the decrease of Al/Cr molar ratios from

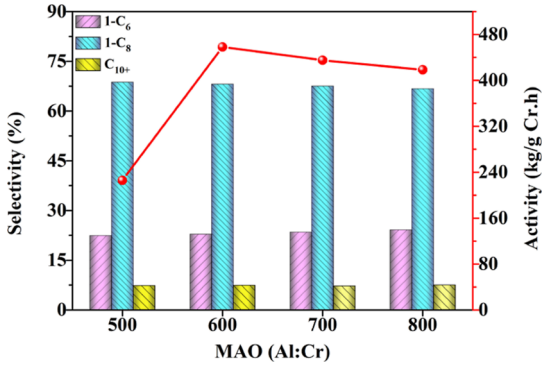

Figure 3. Effects of Al/Cr molar ratios on 1-C_6, 1-C_8, and C_{10+} olefin catalytic performance using the complex 7/MAO system. General conditions: 1.0 L reactor, 10.0 μmol of the catalyst, 45 °C, 45 bar, 180 mL of toluene, and run time: 47 min.

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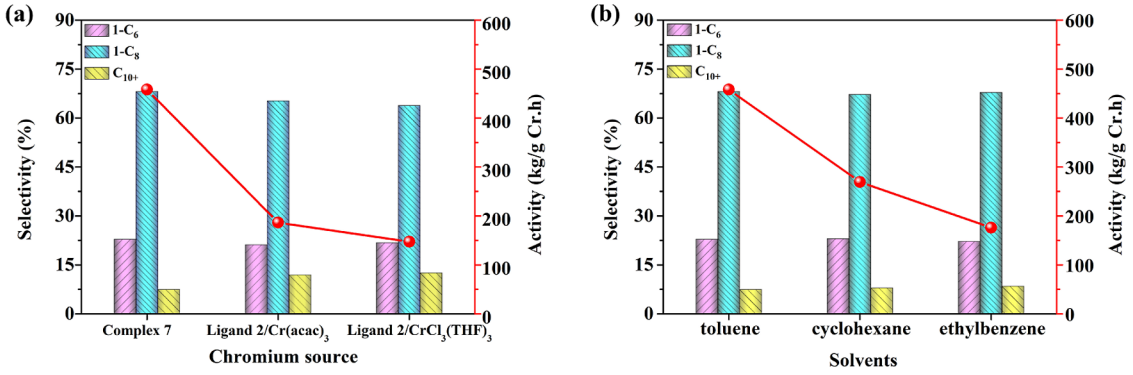

Figure 4. Effects of different Cr sources (a) and solvents (b) on 1-C_6, 1-C_8, and C_{10+} olefin catalytic activity and selectivity using the complex 7/MAO system. General conditions: 1.0 L reactor, 10.0 μmol of the catalyst, 45 °C, 45 bar, Al:Cr = 600, 180 mL of solvent, and run time: 47 min.

600 to 500, the catalytic activity decreased dramatically from 458.2 kg/(g·Cr·h) to 225.8 kg/(g·Cr·h) (Table 3, entries 10−11), indicating the strong influence on activity by MAO.[48] However, at high Al/Cr ratio, i.e., 600−800, the slightly decreased activity was observed as well, in agreement with the literature, which can be attributed to the over-reduced Cr active species caused by extra MAO.[44,49]

It should be noted that both the Cr source and solvent type have the local influences on catalytic ethylene tri/tetramerization.[50] Unlike complex **7** bearing the ligand **2** system, $Cr(acac)_3$ or $CrCl_3(THF)_3$ was stoichiometrically mixed with ligand **2** for preparing the in situ catalysts and then were subjected to evaluating the catalytic ethylene tri/tetramerization performance, as shown in Figure 4a. Experimental results indicated that upon activation by MAO, the activity of complex **7** was remarkably superior to that of the in situ mixed system for ligand **2** with $Cr(acac)_3$ or $CrCl_3(THF)_3$ (Table 3, entries 10 and 12−13). Then, different solvents of cyclohexane, toluene, and ethylbenzene were tested, as displayed in Figure 4b. The results showed that toluene was more suitable than cyclohexane and ethylbenzene (Table 3, entries 10 and 14−15).

4. CONCLUSIONS

In the present study, we have synthesized a series of Cr-based complexes **6**−**10** bearing P,N and P,N,N ligands **1**−**5** and investigated their catalytic performance for selective ethylene tri/tetramerization. In particular, impacts of the chelated mode, carbon spacer, and rigidity of the carbon bridge backbone on catalytic reaction activity and selectivity were investigated. It is found that upon activation by MAO, complexes **6**−**8** with P,N-chelation were effective catalysts for ethylene oligomerization, while complexes **9**−**10** with P,N,N-chelation only catalyzed the ethylene polymerization process. Among them, complex **6** bearing the PC_2N backbone ligand showed catalytic activity for non-selective ethylene oligomerization, while complexes **7** and **8** bearing the PC_3N backbone ligand were both active and selective for ethylene tri/tetramerization. Furthermore, complex **8**, which contains a higher rigidity phenyl ligand backbone, showed slightly higher activity but lower selectivity than complex **7**, which contains a lower rigidity ligand backbone. Overall, after optimizing reaction conditions, at 45 °C and 45 bar, the best catalytic performance was achieved with the complex **7**/MAO system in toluene, where high activity of 458.2 kg/(g·Cr·h), excellent selectivity (1-hexene and 1-octene combined) of 90.9%, and extremely low PE content of 0.1% were obtained. This work can serve as a valuable reference for further design of high-performance catalysts for selective ethylene tri/tetramerization.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c02083.

Crystallographic details of complex **8**·THF, NMR spectrum of ligands **1**−**5**, and GC-FID spectra of the typical oligomerization products (PDF)

Crystallographic details of complex **8**·THF (CIF)

Crystal data and structure refinement of complex **8**·THF. (PDF)

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Notes

The authors declare no competing financial interest.

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