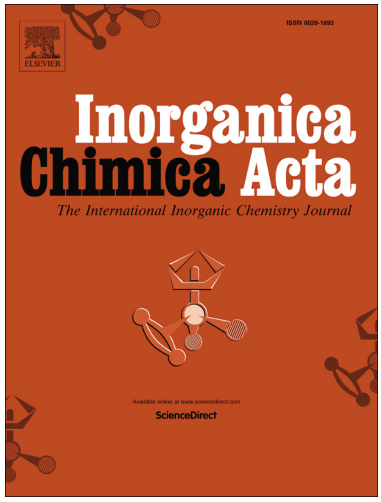

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Highly Active Chromium-Based Selective Ethylene Tri-/Tetramerization Catalysts Supported by *N,N*-Diphospholylamines

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ABSTRACT

We have developed novel Cr(III) catalysts supported by asymmetic N,N-diphospholylamine ligands bearing a phenoxaphosphine group. Upon activation with MMAO-3A, the Cr(III) catalysts supported by the PNP ligands are highly active for ethylene tri-/tetramerization with considerable selectivity. The ligand substitution and oligomerization conditions are found to be essential to achieve high activity and controllable selectivity. The catalytic system with asymmetric diphospholylamine ligands exhibited higher activity than that supported by symmetric ligands. Asymmetric diphospholylamine ligand with a *N*-cyclohexyl group achieved the highest activity of 282.2 kg/(g Cr/h) with a high total selectivity of 83.2 % toward valuable 1-hexene (28.7 %) and 1-octent (54.5 %) at 35 bar under 80 °C.

1. Introduction

In view of the importance of 1-hexene and 1-octene in the production of polyethylene, the selective ethylene tri-/tetramerization have been paid considerable attention from the academic and industrial communities throughout the world in the last two decades.[1-4] Since the first Cr-based catalysts for ethylene trimerization emerged in 1977,[5] only few highly active and selective catalytic systems have been reported for ethylene trimerization[6-22], such as the Phillips pyrrolide,[7] the BP diphosphinoamine,[8] and the Sasol mixed heteroatomic[10] systems. One of us and Hor have also developed Cr(III) catalytic systems with tridentate heteroscorpionate pyrazolyl ligands, exhibiting excellent selectivity (up to 98 wt%) for the production of 1-hexene.[23-25] PCNCP diphosphine ligands[26] and amidine-containing P,N-ligands[27,28] were also been employed in Cr-based ethylene trimerization catalysts. In 2004, through modification of the BP diphosphinoamine ligand (PNP; Fig. 1, **A**), Sasol research group has developed efficient Cr-based ethylene tri-/tetramerization catalysts, where 1-octene selectivity up to 70% was achieved.[29] From then on, it is gaining rapidly increasing attention to develop new Cr catayst supported by different ligand donor set for the tri-/tetramerization processes, most of which are based on the modification of the PNP ligand (**A**) system.[30-34] Numerous studies focused on varying the R substituent on the central nitrogen atom in **A**, but a little attention has been paid to the modification of the P-substituent. Wass and co-workers reported that by in situ combination with $CrCl_3(thf)_3$ and methylaluminoxane (MAO), PNP ligands **B** and **C** containing the dibenzophosphole moiety are active in ethylene polymerization, producing only a very small amount of oligomeric products.[35] However, the structurally related PNP ligands bearing 2,3,4,5-tetraethylphosphole moiety exhibit activity in Cr-catalyzed ethylene oligomerization with excellent selectivity to 1-hexene and 1-octene. The authors proposed that the different catalytic performance of the two kinds of ligands is possibly attributed to the rigidity of the dibenzophosphole moiety.[35]

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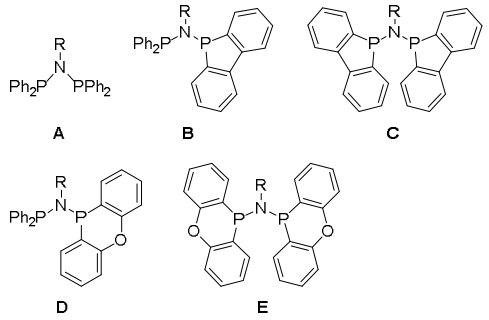


Figure 1. Selected diphophine ligands for selective ethylene tri-/tetramerization.

As part of our studies on the design and synthesis of novel supporting ligands and their application in organometallic catalysis,[36-40] particularly Cr-catalyzed ethylene tri-/tetramerization,[41] we recently reported Cr(III) catalysts supported by PNPO diphosphazane ligand of the type $Ph_2PN(R)P(Ph)OAr$, upon activation with MMAO-3A, are highly active for ethylene tri-/tetramerization with considerable selectivity.[42] Herein, we report for the first time the synthesis of a family of new PNP ligands **D** and **E** generated by replacing one or both PPh_2 groups in ligand **A** with phenoxaphosphine moieties (Fig. 1). The catalytic performance of the new ligands in Cr-catalyzed ethylene tri-/tetramerization was also evaluated.

2. Experimental

2.1. General information

Unless otherwise stated, all reactions and manipulations were performed using standard Schlenk techniques. All solvents were purified by distillation using standard methods. Commercially available reagents were used without further purification. MMAO-3A (modified methylaluminoxane) (7 wt % in heptane solution) was purchased from Akzo-Nobel. NMR spectra were recorded by using a Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (^{1}H NMR $CDCl_3$: 7.26 ppm; ^{13}C NMR $CDCl_3$: 77.0 ppm). Mass spectra were recorded on the HP-5989 instrument by ESI methods. Quantitative gas chromatographic analysis of the products of oligomerization was performed on an Agilent 6890 Series GC instrument with a J&W DB-1 column working at 36 °C for 10 min and then heating at 10 °C min−1 until 250 °C. n-Nonane was used as an internal standard. X-ray diffraction analysis was performed by using a Bruker Smart-1000X-ray diffractometer. 10-chlorophenoxahosphine, $Ph_2PN(^iPr)H$ and $Ph_2PN(Cy)H$ are known compounds, and were prepared according to modified literature methods, respectively.[43,44] Their spectra were consistent with that of the published data.

2.2. Synthesis of of ligand L^1*:*

In a representative procedure, 2.6 mL of n-butyllithium (1.6 M in hexanes. 4.11 mmol) was added dropwise at 0 °C to a stirred solution of 1.0 g of $Ph_2PN(iPr)H$ (4.11 mmol) in 15 mL of toluene. The reaction mixture was stirred for 30 min. Next, at 0 °C a solution of 10-chlorophenoxahosphine (730 mg, 4.11 mmol) in 15 mL of toluene was added, and the reaction mixture was stirred for 4 h. The solvent was removed under vacuum. The crude product was purified by column chromatography (silica gel; v/v, PE/ EtOAc = 20:1) to afford $\mathbf{L^1}$ (285 mg ,15.7%). ^{1}H NMR (400 MHz, $CDCl_3$) : δ = 7.42-7.38 (m, 3H), 7.29-7.28 (m, 6H), 7.22-7.20 (m, 6H), 7.11-7.07 (m, 3H), 3.37-3.28 (m, 1H), 1.02 (d, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) : δ = 155.3, 135.5, 135.1, 132.8, 132.6, 131.1, 131.1, 130.8, 130.6, 129.0, 128.8, 128.4, 127.9, 127.9, 123.0, 122.9, 117.7, 51.6, 24.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ = -16.1, -1.1 (br). HRMS (ESI): m/z $[M + H]^+$ calcd. for $C_{27}H_{26}NOP_2^+$: 442.1490; found: 442.1487; Anal. Calcd. for $C_{27}H_{25}NOP_2$ (%): C, 73.46; H, 5.71; N, 3.17; found: C, 73.51; H, 5.78; N, 3.39.

2.3. Synthesis of ligand L^2*:*

$\mathbf{L^2}$ has been prepared similarly to $\mathbf{L^1}$ with yield of 11.8%, starting fromn-butyl lithium (1.6 M in hexanes. 4.11 mmol), $Ph_2PN(Cy)H$ (100 mg, 0.20 mmol) and 10-chlorophenoxahos -phine (730 mg, 4.11 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) : δ = 7.42-7.38 (m, 2H), 7.28-7.21 (m, 14H), 7.11-7.08 (m, 2H), 2.87-2.81 (m, 1H), 1.82-1.79 (m, 2H), 1.60-1.57 (m, 3H), 0.98-0.85 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) : δ = 155.2, 135.6, 135.2, 132.7, 132.5, 131.1, 128.4, 127.9, 127.8, 123.0, 122.9, 117.6, 59.9, 35.5, 26.3, 25.4. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 1.1, 56.3 (br). HRMS (ESI): m/z $[M + H]^+$ calcd. for $C_{30}H_{30}NOP_2^+$: 482.1803, found: 482.1808; Anal. Calcd. for $C_{30}H_{29}NOP_2$ (%): C, 74.83; H, 6.07; N, 2.91; found: C, 74.67; H, 6.33; N, 3.19.

2.4. Synthesis of ligand L^3*:*

At 0 °C Et_3N (2.3 mL，11.08 mmol) was added dropwise to a solution of 10-chlorophenoxahosphine (731 mg, 4.11 mmol) in 15 mL of dichloromethane and the reaction mixture was stirred for 10 min. Then isopropylamine (0.17 mL，1.94 mmol) was added, and the reaction mixture was stirred for 4-5 h. All volatiles were removed under vacuum, and the rude product was purified by column chromatography using silica gel (v/v, PE/ EtOAc = 20:1) to afford the $\mathbf{L^3}$ as a white solid (224 mg, 12.7%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.38 (m, 4H), 7.20-7.18 (m, 4H), 7.06-6.94 (m, 4H), 6.92-6.85 (m, 4H), 3.02-2.88 (m, 1H), 0.91 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.7, 135.3, 135.0, 131.1, 123.0, 122.9, 117.6, 51.1, 24.5. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 3.1 (br).

HRMS (ESI): m/z $[M + H]^+$ calcd. for $C_{27}H_{24}NO_2P_2^+$: 456.1282, found: 456.1277; Anal. Calcd. for $C_{27}H_{23}NO_2P_2$ (%): C, 71.21; H, 5.09; N, 3.08; found: C, 70.97; H, 5.19; N, 3.10.

2.5. Synthesis of ligand ***L*** ^{4}*:*

L^{4} has been prepared similarly to **L**^{3} with yield of 11.8%, starting from Et_3N (2.3 mL, 16.10 mmol), cyclohexylamine (100 mg, 0.20 mmol) and 10-chlorophenoxahosphine (1.0 g, 4.26 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39-6.55 (m, 16H), 2.49-2.43 (m, 1H), 1.77-1.68 (m, 2H), 1.55-1.43 (m, 2H), 1.05-1.01 (m, 1H), 0.98-0.77 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.7, 135.5, 135.1, 131.1, 122.9, 122.8, 117.5, 59.5, 35.4, 26.4, 25.3. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 3.7 (br). HRMS (ESI): m/z $[M + H]^+$ calcd. for $C_{30}H_{28}NO_2P_2^+$: 496.1595, found: 496.1587; Anal. Calcd. for $C_{30}H_{27}NO_2P_2$ (%): C, 72.72; H, 5.49; N, 2.83; found: C, 72.61; H, 5.55; N, 2.84.

2.6 Synthesis of Pd complex ***1***

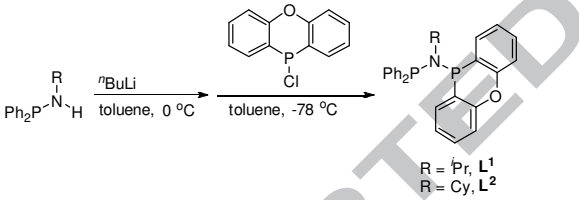
The mixture of **L**^{1} (50 mg, 0.113 mmol) and $Pd(CH_3CN)_2Cl_2$ (29.23 mg, 0.11 mmol) was stirred in the DCM (3.0 mL) at room temperature for 4-5 h. All volatiles were removed under vacuum, and the rude product was washed twice with petroleum ether to afford pure 1 as a yellow solid (45 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) : δ = 8.30-8.28 (m, 2H), 8.26-8.23 (m, 4H), 8.01-7.96 (m, 4H), 7.74-7.68 (m, 4H), 7.63-7.59 (m, 2H), 7.45-7.35 (m, 2H), 3.31-3.19 (m, 1H), 0.40 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9, 135.8, 134.5, 134.3, 133.5, 133.4, 129.7, 129.6, 125.4, 125.3, 119.0, 54.1, 29.7. ^{31}P NMR (162 MHz, $CDCl_3$) : δ = 34.3 (d, *J* = 25.9 Hz), -10.0 (d, *J* = 25.9 Hz). HRMS (ESI): m/z [M] calcd. for $C_{27}H_{25}Cl_2NO_2P_2Pd$: 616.9823; found: 616.9820.

2.7 Oligomerization of ethylene

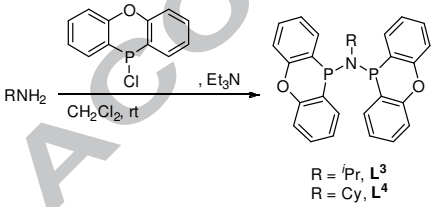
A 120 mL stainless steel reactor was dried at 120 °C for 3 h under vacuum, and then cooled down to the desired reaction temperature. The precatalysts and co-catalysts (MMAO) were combined in a Schlenk vessel in the ratios indicated in Table 1. The resultant mixture was stirred for 1 min and immediately transferred to the reactor. Then the reactor was immediately pressurized. After the specified reaction time, the reaction was stopped by shutting off the ethylene feed, cooling the system at 0 °C, depressurizing, and quenched by addition of 30 mL of 10% aq. HCl. A small sample of the upper-layer solution was filtered through a layer of Celite and analysed by GC using nonane as the internal standard. The individual oligomerization products were identified by GC-MS. The remainder of the upper-layer solution was filtered to isolate the solid polymeric products. The solid products were suspended in 10% aq. HCl and stirred for 24 h, dried under reduced pressure and weighed.

3. Results and discussion

Asymmetric diphosphine ligands **L**^{1} and **L**^{2} having two phenoxaphosphine groups were synthesized by a reaction of in-situ prepared Ph_2PNRLi with one equivalent of phenoxaphosphinous chloride[45] (Scheme 1). Symmetric diphosphine ligands **L**^{3} and **L**^{4} were prepared by the treatment of RNH_2 with two equivalents of phenoxaphosphinous chloride in the presence of Et_3N (Scheme 2).

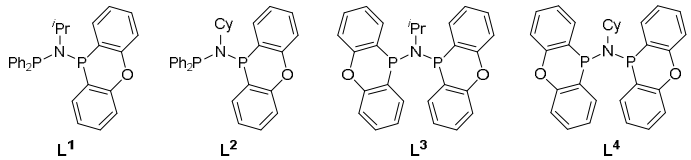


Scheme 1. Synthesis of asymmetric diphosphine ligands **L**^{1} and **L**^{2}



Scheme 2. Synthesis of symmetric diphosphine ligands **L**^{3} and **L**^{4}

Table 1. Ethylene oligomerization with PNP ligands **L**^{1}**~L**^{4} in conjunction with chromium source and MMAO[a]



Entry (Ligand)	Activity (kg/g Cr/h)	Oligomer distribution (wt%)						PE (wt%)[c]
		1-C_6 (wt%)[b]	1-C_6 in C_6 (%)	cy-C_6 (wt%)[b]	1-C_8 (wt%)[b]	1-C_8 in C_8 (%)	C_{10+} (wt%)[b]	
1 ($\mathbf{L^1}$)	102.0	20.1	62.7	8.5	60.8	99.6	6.8	10.1
2 ($\mathbf{L^2}$)	232.3	21.7	85.9	3.5	60.8	99.8	13.8	6.6
3 ($\mathbf{L^3}$)	32.9	17.7	43.5	20.5	53.6	98.9	5.2	1.2
4 ($\mathbf{L^4}$)	27.6	10.6	23.5	34.5	44.4	99.6	10.5	11.1
5 ($\mathbf{L^1}$)[d]	81.5	13.2	58.7	9.3	66.9	99.8	10.5	5.2
6 ($\mathbf{L^2}$)[d]	102.3	15.7	62.7	9.4	63.9	99.8	10.9	2.4
7 ($\mathbf{L^2}$)[e]	54.1	10.4	20.8	39.8	36.0	98.4	13.1	12.0

[a] Conditions: 2.5 μmol $Cr(acac)_3$, 1.2 equiv ligand, 600 equiv. MMAO-3A, 35 bar of ethylene, 30 mL methylcyclohexane, 60°C, 30 min. [b] wt % of liquid products (oligomers). [c] wt % of total product (oligomers+polymer). [d] 2.5 μmol $CrCl_3(THF)_3$, 1.2 equiv ligand. [e] 30 mL toluene as solvent.

The ligands $\mathbf{L^1}$~$\mathbf{L^4}$ were examined for ethylene oligomerization in conjunction with $Cr(acac)_3$ or $Cr(THF)_3Cl_3$ upon activation with MMAO, and the results are summarized in Table 1.

Upon activation of 600 molar excess of MMAO, all of the Cr precatalysts supported by diphosphine ligands ($\mathbf{L^1}$~$\mathbf{L^4}$) were active in selective tri-/tetramerization reaction at 35 bar ethylene and 60 °C. Increasing steric bulk of N-alkyl group by replacing of the isopropyl group in $\mathbf{L^1}$ with a cyclohexyl group in $\mathbf{L^2}$ dramatically enhanced the activity with similar selectivity toward both 1-hexene and 1-octene, and less polymer was observed when using ligand $\mathbf{L^2}$ (Table 1, entries 1 and 2). Compared with the catalytic systems with asymmetric $\mathbf{L^1}$ and $\mathbf{L^2}$, using those supported by symmetric ligands $\mathbf{L^3}$ and $\mathbf{L^4}$ led a significant decrease in activity, and produced less 1-hexene and 1-octene and more undesirable cyclic C_6 products, respectively (Table 1, entries 3 and 4). The low activities of the catalysts supported by symmetric ligands $\mathbf{L^3}$ and $\mathbf{L^4}$ are probably due to the rigidity of the two phenoxaphosphine moieties in them.

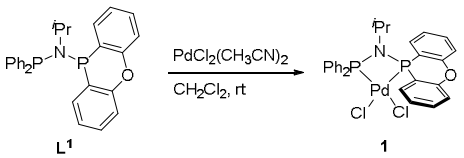
Asymmetric ligands $\mathbf{L^1}$ and ligand $\mathbf{L^2}$ achieved higher activities by using $Cr(acac)_3$ as Cr source than by using $CrCl_3(THF)_3$ (Table 1, entries 1, 2, 5 and 6). Reaction solvent had remarkable impact on the catalytic behavior in this catalyst system. $\mathbf{L^2}$ in methylcyclohexane exhibited much higher activity and selectivity toward 1-hexene and 1-octene than those achieved in toluene (Table 1, entries 2 and 7).

Table 2. Catalyst performance of $Cr(acac)_3$/PNP ligands $\mathbf{L^1}$ and $\mathbf{L^2}$ in methylcyclohexane[a]

Entry (Ligand)	Al/Cr	T (°C)	Activity (kg/g Cr/h)	Oligomer distribution (wt%)						PE (wt%)[c]
				1-C_6 (wt%)[b]	1-C_6 in C_6 (%)	cy-C_6 (wt%)[b]	1-C_8 (wt%)[b]	1-C_8 in C_8 (%)	C_{10+} (wt%)[b]	
1 (**L**^{1})	600	80	147.7	29.1	81.1	6.8	53.7	99.8	10.4	4.6
2 (**L**^{2})	600	80	282.2	28.7	89.1	3.5	54.5	99.8	13.2	6.6
3 (**L**^{2})[d]	600	60	101.5	15.6	65.2	8.3	64.0	99.7	11.8	4.5
4 (**L**^{2})	400	60	75.5	15.3	65.1	8.2	64.3	99.6	12.0	10.9
5 (**L**^{2})	800	60	235.3	21.1	80.3	5.1	59.9	99.8	13.8	3.8

[a] Conditions: 2.5 μmol $Cr(acac)_3$, 1.2 equiv ligand, 35 bar of ethylene, 30 mL methylcyclohexane, 30 min. [b] wt % of liquid products (oligomers). [c] wt % of total product (oligomers+polymer). [d] 25 bar of ethylene.

In general, the catalytic activity and selectivity for ethylene oligomerization were significantly influenced by the reaction conditions, such as Al/Cr ratio, temperature etc. Aimed to improve the catalyst performance, **L**^{1} and **L**^{2} were chosen for further investigation under different reaction conditions. The results are shown in the Table 2. For **L**^{1} and **L**^{2}, increasing temperature from 60 to 80 °C led to an increase in activity and selectivity toward 1-hexene, and a decrease in the 1-octene selectivity (Table 2, entries 1 and 2). **L**^{2} achieved the highest activity of 282.2 kg/(g Cr/h) with a high total selectivity of 83.2 % toward valuable 1-hexene (28.7 %) and 1-octent (54.5 %) at 35 bar under 80 °C (Table 2, entry 2). For **L**^{2}, decreasing ethylene pressure from 35 to 25 bar causes a dramatic decrease in activity (Table 2, entry 3). The effect of Al/Cr ratio on the catalytic performance of the Cr catalyst supported by **L**^{2} was further investigated. Lowering the amount of MMAO to 400 equiv led to a decrease in activity for **L**^{3} and produced more polymer formation (Table 2, entry 4). Increasing the Al/Cr molar ratio from 600 to 800 enhanced slightly the activities and produced less polymer formation (Table 2, entry 5).



Scheme 3. Synthesis of Pd Complex **1** Based on Ligand **L**^{1}

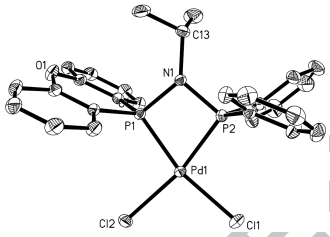


Figure 2. Molecular structure of **1** with 20% probability. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)-P(2) 2.2089(13); Pd(1)-P(1) 2.2133(11); Pd(1)-Cl(1) 2.3533(12); Pd(1)-Cl(2) 2.3573(13); P(2)-Pd(1)-P(1) 71.73(5); P(2)-Pd(1)-Cl(1) 95.07(5); P(1)-Pd(1)-Cl(1) 166.28(3); P(2)-Pd(1)-Cl(2) 167.79(3); P(1)-Pd(1)-Cl(2) 97.06(5); Cl(1)-Pd(1)-Cl(2) 96.40(6); P(2)-N(1)-P(1) 100.06(14)

We next investigated the coordination mode of the novel PNP diphosphine ligands. After massive attempts to isolate single crystals of Cr complexes ligated by $\mathbf{L^1}$~$\mathbf{L^2}$ failed, we managed to obtain a single crystal of their counterpart palladium complex **1** suitable for X-ray diffraction analysis (Scheme 3 and Fig. 2) Pd complex **1**, prepared by the reaction of L1 with $PdCl_2(MeCN)_2$, adopts a regular square-planar coordination mode, involving two P atoms and two Cl atoms. This kind of coordination mode is typically observed in other comparable symmetric PNP-Pd complexes.[46-48] In the coordination environment, the Pd–P bond lengths are 2.2089(13) and 2.2133(11) Å, respectively. Pd complex 1 has an acute P(1)–Pd–P(2) coordination angle (71.73(5)). The phenoxaphosphine group of **1** is directed away from the metal.

4. Conclusion

In summery, novel PNP ligand bearing phenoxaphosphine group have been synthesized. Upon activation with MMAO-3A, the Cr(III) catalysts supported by the PNP ligands are highly active for ethylene tri-/tetramerization with considerable selectivity. The ligand substitution and oligomerization conditions are found to be essential to achieve high activity and controllable selectivity. The catalytic system with asymmetric L^1 and $\mathbf{L^2}$ exhibited higher activity than that supported by symmetric ligands $\mathbf{L^3}$ and $\mathbf{L^4}$. Asymmetric $\mathbf{L^2}$ with a N-cyclohexyl group achieved the highest activity of 282.2 kg/(g Cr/h) with a high total selectivity of 83.2 % toward valuable 1-hexene (28.7 %) and 1-octent (54.5 %) at 35 bar under 80 ^{o}C. The Pd complex **1** ligated by $\mathbf{L^1}$ adopts a regular square-planar coordination mode, involving two P atoms and two Cl atoms.

Acknowledgment

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2017.

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Highly active Chromium-Based Selective Ethylene Tri-/Tetramerization Catalysts Supported by *N,N*-Diphospholylamines

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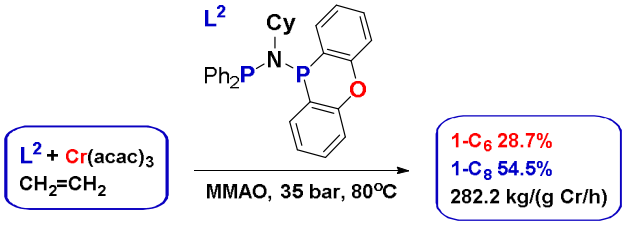

Cr(III) catalysts supported by asymmetic *N,N*-diphospholylamine ligands bearing a phenoxaphosphine group are highly active for ethylene tri-/tetramerization with considerable selectivity upon activation with MMAO-3A. Asymmetric PNP ligand with a *N*- cyclohexyl group achieved the highest activity of 282.2 kg/(g Cr/h) with a high total selectivity of 83.2 % toward valuable 1-hexene (28.7 %) and 1-octene (54.5 %) at 35 bar under 80 °C.