ACS Catalysis

Research Article

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Switchable Ethylene Tri-/Tetramerization with High Activity: Subtle Effect Presented by Backbone-Substituent of Carbon-Bridged Diphosphine Ligands

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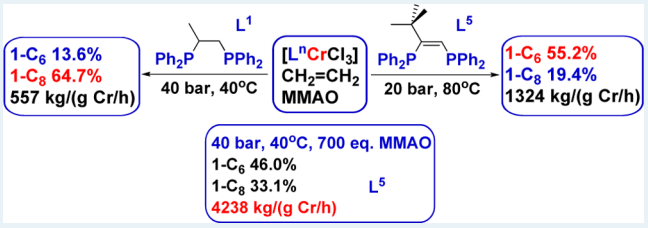
Supporting Information

ABSTRACT: The effect of backbone-substituent of carbon-bridged diphosphine ligands of the types $\{Ph_2PCH(R)-CH_2PPh_2\}$ and $\{Ph_2PC(R)=CHPPh_2\}$ on the catalyst performance in ethylene oligomerization has been explored. Cr complex bearing a methyl-substituted diphosphine ligand with saturated linker exhibited the highest selectivity of 64.7% toward 1-octene. Cr complex bearing a tert-butyl-substituted diphosphine ligand with unsaturated linker showed a high activity of 4238 kg/(g Cr/h) at 40 bar and 40 °C and achieved a high total selectivity of 79.1% toward valuable 1-hexene and 1-octene. The 1-hexene selectivity could be improved up to 55.2% (19.4% 1-octene) at 20 bar and 80 °C. Some of the new complexes are even more active than the well-known most efficient ethylene tri/tetramerization catalyst systems.



KEYWORDS: *ethylene trimerization, ethylene tetramerization, backbone-substituent, diphosphine ligand, chromium(III) catalysts*

INTRODUCTION

The oligomerization of ethylene generally gives a broad distribution of α-olefins which requires fractional distillation of the products to give relatively low yields of the desired fractions. To meet demand growth for 1-hexene and 1-octene, the selective ethylene tri/tetramerization has received a great deal of attention from the academic and industrial communities throughout the world in the last two decades.[1] Although this was first achieved with Cr-based catalysts in 1977,[2] there are few highly active and selective catalysts for ethylene trimerization[3] and they include the Phillips pyrrolide,[3a,b] the BP diphosphinoamine,[3c] and the Sasol mixed heteroatomic[3d] systems. Recently, one of us and Hor have developed Cr(III) catalytic systems with a variety of tridentate heteroscorpionate pyrazolyl ligands, exhibiting excellent selectivity (up to 98 wt %) for ethylene trimerization.[4] Other diphosphine ligands[5] and P,N-ligands[6] have also been used in Cr-based ethylene trimerization catalysts.

In 2004, by modification of the BP diphosphinoamine (PNP) ligand **A** (R = Me, Ar = *o*-OMe-Phenyl) (Figure 1), the researchers from Sasol found removing *ortho*-substitution from the phosphine phenyl groups and increasing the steric bulk of the N-substituent from methyl group to isopropyl group cause a switch in selectivity from 1-hexene to 1-octene.[7] 1-Octene selectivity up to 70% was achieved using PNP ligand **A** (R = ^{i}Pr, Ar = Ph) at 45 bar. A further increase in steric bulk of the N-substituent enhances the combined selectivity toward the two desired products (1-hexene and 1-octene) while lowering the 1-octene/1-hexene ratio.[8] Thus, the C_6 selectivity ranged from 13% using *N*-isopropyl PNP ligand to 41% using the more bulky *N*-2,6-dimethylcyclohexyl PNP ligand, while C_8 selectivity decreased from 70% to 48%. Recently, several carbon-bridged diphosphine ligands including **B**, **C**, and **D** were also found to be active in Cr-catalyzed tri/tetramerization catalysts (Figure 1).[9] For these carbon-bridged diphosphine ligands, bridge unsaturation and the rigidity of backbone also significantly affect catalyst performance. Cr complex based on the bis(diphenylphosphino)benzene ligand **B** exhibited very

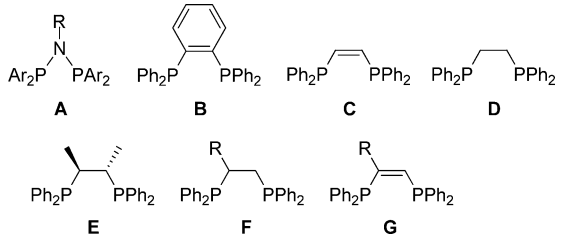


Figure 1. Selected diphosphine ligands **A**–**E** in Cr-catalyzed ethylene tri/tetramerization and targeted carbon-bridged diphosphine ligands **F** and **G**.

Received: August 6, 2013
Revised: September 2, 2013
Published: September 18, 2013

   dx.doi.org/10.1021/cs400651h | *ACS Catal.* 2013, 3, 2311–2317

high activity toward tri/tetramerization and is among the most active ethylene tri/tetramerization catalyst systems, which is much more active than those bearing **C**, **D**, and even typical PNP ligand **A**.[9] Most modifications of these carbon-bridged diphosphines have been made on the length of carbon-bridge and very few on their backbone substitution. Kang and researchers from S-K Energy reported a series of bis-(diphenylphosphino) ethane **E** with a dimethyl-substituted chiral backbone for selective ethylene tetramerization.[10] Compared to Cr catalyst based on the related ligand **D** with no substituent on its backbone, the Cr complex of ligand **E** exhibited enhanced selectivity toward ethylene tetramerization and showed very high activity. However, although various efficient ethylene tri/tetramerization catalyst systems have been established,[11] achieving very high activity without compromising total selectivity toward valuable 1-hexene and 1-octene has remained a challenge. Only a few catalyst systems could achieve industrially acceptable high activity, such as the Sasol's PNP (**A**), S-K Energy's diphosphine (**E**), and bis-(diphenylphosphino)benzene (**B**) catalytic systems. Very surprisingly, there is no asymmetric carbon-bridged diphosphine ligand reported for ethylene tri/tetramerization up to now, though those carbon-bridged diphosphine ligands, such as **B** and **E**, have been proved to be particularly promising. With our aim of understanding well the influence of ligand structure on catalyst performance in ethylene oligomerization,[4,12] we decided to explore the influence of backbone-substituent of diphosphine ligands of type **C** and **D**. We herein report our study on two kinds of asymmetric carbon-bridged diphosphine ligands with one substituent on their backbones, i.e., bis-(diphenylphosphino) ethane with a saturated linker (**F**) and bis(diphenylphosphino) ethene with an unsaturated linker (**G**). In this study, we establish an ethylene tri/tetramerization catalyst system with a high activity of up to 4238 kg/(g Cr/h) and a high total selectivity of up to 80% toward 1-hexene and 1-octene, and a new insight into the subtle effect of varying the backbone-substituent on the overall oligomerization performance and in particular on the selectivity was also presented.

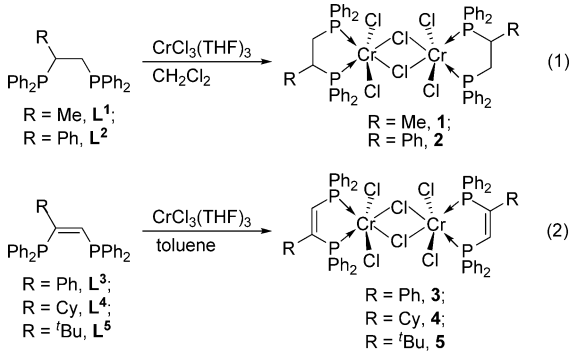
RESULTS AND DISCUSSION

Asymmetric carbon-bridged diphosphine ligands of the type $\{Ar_2PCH(R)CH_2PAr_2\}$ ($\mathbf{L^1}$–$\mathbf{L^2}$) and $\{Ar_2PC(R)=CHPAr_2\}$ ($\mathbf{L^3}$–$\mathbf{L^5}$) were simply prepared by two-step synthesis from commerially available alkynes or diols according to literature methods.[13,14] Treatment of the diphosphine ligands $\mathbf{L^1}$–$\mathbf{L^5}$ with $[CrCl_3(THF)_3]$ in CH_2Cl_2 or toluene afforded the corresponding Cr(III) complexes **1**–**5** (Scheme 1). The Cr complexes, **1**–**5**, were not structurally characterized due to failure to obtain the single crystals suitable for X-ray analysis but are proposed to adopt the chloride bridged dinuclear structures as those found in other known related Cr complexes bearing carbon-bridged diphosphines such as **B**, **C**, **D**, and **E** (Figure 1).[9,10]

To investigate the effect of backbone-substituent of ligands $\mathbf{L^1}$–$\mathbf{L^5}$ on catalyst performance, Cr complexes **1**–**5** were taken for catalytic testing. The results, with a comparison against the known efficient Cr precatalysts (**6**–**8**) based on diphosphine ligands, i.e., $Ph_2PN(^iPr)PPh_2$ ($\mathbf{L^6}$), $Ph_2P(C_6H_4)PPh_2$ ($\mathbf{L^7}$), and $Ph_2P\{CH(Me)CH(Me)\}PPh_2$ ($\mathbf{L^8}$), and those Cr precatalysts (**9**, **10**) bearing related ligands $Ph_2P(CH=CH)PPh_2$ ($\mathbf{L^9}$) and $Ph_2P(CH_2CH_2)PPh_2$ ($\mathbf{L^{10}}$) (Figure 2), are summarized in Table 1.

At 40 bar ethylene and 40 °C and in the presence of 500 molar excess of MMAO-3A, all of the precatalysts (**1**–**5**) bearing carbon-bridged diphosphine ligands were highly active in the selective tri/tetramerization reaction. Precatalyst **1** bearing diphosphine ligand with saturated linker exhibited the highest selectivity of 64.7% toward 1-octene with considerable activity of 577 kg/(g Cr/h) (Table 1, entry 1). Increasing the steric bulk of backbone-subsituent by replacement of the methyl group (in **1**) with a phenyl group (in **2**) enhanced the activity and led to more production of 1-hexene at the expense of 1-octene, and more polymer was observed when using **2** (Table 1, entries 1 and 2). Very high activities (1900 kg/(g Cr/h) for **4**, and 1926 kg/(g Cr/h) for **5**) were obtained using precatalysts **4** and **5** bearing diphosphine ligands with unsaturated linkers, which are more active than the precatalyst **3** bearing less bulky backbone-substituent (phenyl group) (Table 1, entries 3–5). It is worth noting that the amount of polymer obtained by **4** and **5** was much less than that when using **1** and **2**. These results indicate that backbone-substituent and/or ligand rigidity play an important role in catalyst performance. Under the same reaction condition, the activities achieved by **4** and **5** even surpass those obtained by the most efficient catalyst systems (Table 1, entries 9–11), such as **6** bearing a PNP ligand, **7** bearing a bis(diphenylphosphino)-benzene ligand, and **8** bearing a carbon-bridged diphosphine ligand with two chiral backbone-substituents, while the selectivities to 1-octene were lower than that using precatalyst **7**. Since the reactor was almost full after runing the oligomerization reaction for 30 min when using **4** and **5** (Table 1, entries 4 and 6), the reaction was then terminated after 15 min. In shorter reaction time, **5** bearing bulkier ^{t}Bu backbone-substituent exhibited very high activities of 3277 kg/(g Cr·h), which is more active than cyclohexyl-substituted complex **4** (Table 1, entries 5 and 7). Precatalyst **5** retained high activity even at low catalyst concentration (0.6 μmol in 30

Scheme 1. Synthesis of Cr Complexes 1–5 Based on Carbon-Bridged Diphosphine Ligands $\mathbf{L^1}$–$\mathbf{L^5}$



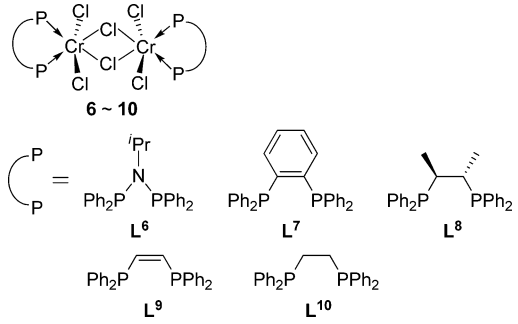


Figure 2. Known Cr precatalysts **6**–**10** bearing diphosphine ligands $\mathbf{L^6}$–$\mathbf{L^{10}}$ chosen for comparison.

dx.doi.org/10.1021/cs400651h | ACS Catal. 2013, 3, 2311–2317

Table 1. Ethylene Oligomerization with New Complexes 1−5 and Complexes 6−10[a]

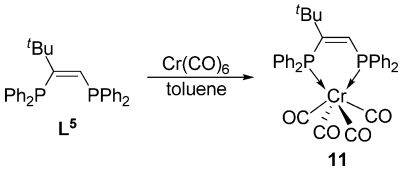
			oligomer distribution (wt %)						
entry (cat.)	yield (g)	activity (kg/g Cr/h)	1-C_6 (wt %)[b]	1-C_6 in C_6 (%)	cy-C_6 (wt %)[b]	1-C_8 (wt %)[b]	1-C_8 in C_8 (%)	C_{10+} (wt %)[b]	PE (wt %)[c]
1 (**1**)	15.0	577	13.6	55.5	10.4	64.7	99.2	9.1	3.3
2 (**2**)	24.4	937	28.9	74.2	9.9	53.6	98.9	8.3	5.8
3 (**3**)	25.6	984	17.6	49.7	17.5	52.5	98.2	9.2	0.8
4 (**4**)	49.4	1900	23.1	61.4	14.3	50.3	98.1	11.5	0.8
5 (**4**)[d]	27.4	2105	24.2	63.4	13.8	51.4	99.4	9.7	0.2
6 (**5**)	50.1	1926	39.8	83.1	8.1	40.4	98.6	11.3	0.1
7 (**5**)[d]	42.6	3277	40.7	82.6	8.2	39.5	99.0	10.6	0.3
8 (**5**)[e]	14.9	1908	24.7	66.6	12.2	55.3	99.6	6.8	0.9
9 (**6**)	7.9	305	9.2	63.8	5.2	72.7	99.2	10.2	1.7
10 (**7**)	43.2	1660	23.0	66.5	11.3	53.0	98.6	11.5	1.1
11 (**8**)	40.4	1552	33.4	89.3	4.0	52.9	99.5	9.4	0.7
12 (**9**)[f]		144	15.7		8.7	59.3			4.9
13 (**10**)[f]		303	7.3		17.3	46.7			5.2

[a]Conditions: 120 mL reactor, 1.0 μmol of precatalyst, 500 equiv. of MMAO-3A, 40 bar of ethylene, 30 mL of methylcyclohexane, 40 °C, 30 min. [b]wt % of liquid products (oligomers). [c]wt % of total product (oligomers + polymer). [d]15 min. [e]0.6 μmol of precatalyst. [f]50 bar of ethylene, 60 °C, taken from ref 9.

mL of methylcyclohexane) (Table 1, entry 8). Poor activities were obtained using the related precatalysts **9** and **10** bearing carbon-bridged diphosphine ligands without backbone-subsituent (Table 1, entries 12 and 13).[11] It suggests the significant influence of backbone-subsituent in these carbon-bridged diphosphine ligands on the outcome of the catalysis.

For the precatalysts **1**−**5**, increasing the steric bulk of backbone-subsituent leads to lowering the 1-octene/1-hexene ratio and producing more 1-hexene. The selectivity trend is similar to those reported for the PNP ligand catalyst system, where increasing the steric bulk of N-subsituent also leads to a decrease in the 1-octene/1-hexene ratio. In order to establish the coordination mode of the carbon-bridged diphosphine ligands and thus to understand well the subtle effect presented by backbone-substituent on the catalyst preformance, Cr complex based on ligand $\mathbf{L}^5$ was selected for structural analysis by single-crystal X-ray diffraction. Reaction of $\mathbf{L}^5$ with $[Cr(CO)_6]$ under reflux in toluene led to the formation of the desired $[Cr(CO)_4(\mathbf{L}^5)]$ (**11**) (Scheme 2). Single crystals,

Scheme 2. Synthesis of Cr Complexes 11 Based on Ligand $\mathbf{L}^5$



suitable for X-ray diffraction study, were obtained by slow diffusion of *n*-hexane into CH_2Cl_2 solution of **11**, and the structure is illustrated in Figure 3. Complex **11** crystallizes with two molecules in the asymmetric unit where the two crystallographically independent molecules adopt similar conformations. Complex **11** displays a distorted-octahedral geometry with an expected planar Cr−P−C−C−P ring. In **11**, the repulsion between the backbone-substituent tert-butyl group and adjacent phosphine phenyl groups results in a smaller $P^1-C^1-C^2$ angle (113.3°), compared to another $P^2-C^2-C^1$ angle (122.4°), and thus a smaller $C^{Ph}-P^1-Cr$ angle (average, 113.9°), compared to another $C^{Ph}-P^2-Cr$ angle (average, 119.0°).

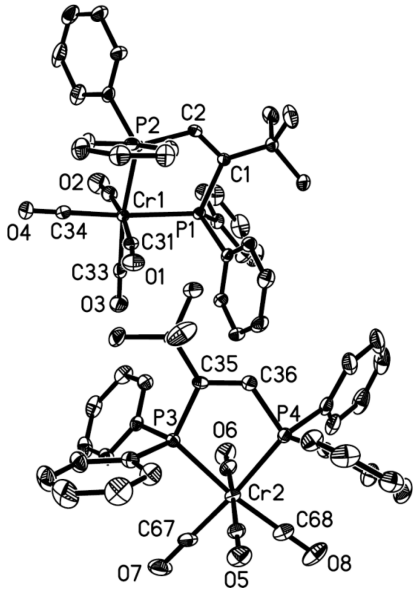


Figure 3. Molecular structure of Cr complex **11**.

Complex **11** has a larger bite angle than the PNP ligand in **12**, but a smaller $C^{Ph}-P-Cr$ angle is found in **11** (Figure 4).[15] This is expected to be highly relevant to the lower 1-octene/1-hexene ratio and the very high activitiy achieved by **5**. The effect presented by backbone-substituent could be well understood by taking the steric environment around the catalyst center into account. Figure 5 depicts possible reaction intermediates and shows the proposed steric interactions between diphosphine ligands and the growing metallacycle. For the PNP−Cr catalyst system, the lowest 1-hexene/1-octene ratio of 1:1 was achieved when using *N*-2,6-dimethylcyclohexyl PNP ligand ($\mathbf{L}^{PNP}$, Figure 5).[8d] The authors assumed that introducing a second methyl group in the *N*-cyclohexyl group of PNP ligand leads to more pronounced interactions between the methyl group with the catalyst center. As chromacyclononane is sterically more demanding than chromacycloheptane, the increased steric interaction in the intermediate causes the coordination of ethylene to a seven-membered chromacyclic intermediate unfavorable, which thus leads to lower 1-octene/

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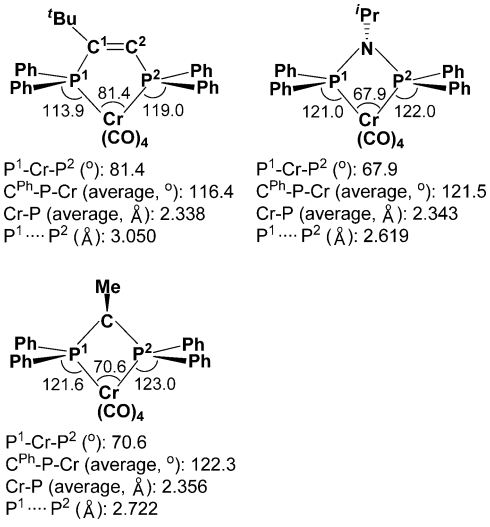

Figure 4. Comparison of molecular structure of complex **11** with related complexes $[Cr(CO)_4(L^6)]$ (**12**)[15] and $[Cr(CO)_4(L^{PCP})]$ (L^{PCP} = $Ph_2PC(Me)PPh_2$, **13**).[16]

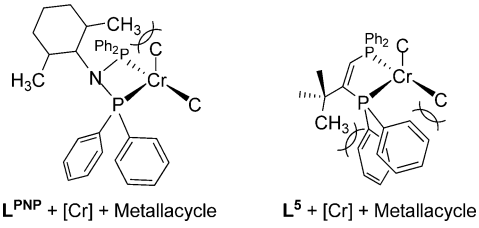

Figure 5. Proposed steric interactions between ligand and metallacycle (L^{PNP} = Ph_2PN(2,6-dimethylcyclohexyl)PPh_2).

1-hexene ratio and form more 1-hexene. In the case of complexes **3**–**5**, the introduction of bulky ^{t}Bu backbone-substituent in **5** leads to more repulsion between backbone-substituent and the adjacent phosphine phenyl groups, which leads to more steric crowding around the catalytic center, and then results in a shift toward 1-hexene formation. The repulsion effect could be confirmed by the observation of a smaller C^{Ph}–P^1–Cr angle in **11**. It is worth noting that the smaller C^{Ph}–P^1–Cr angle could also offer more protection for the active metal center during the catalytic process, which probably attributes to the very high catalytic activity achieved by **5**. Compared to **12**, complex **13** bearing a PCP ligand (dppm) has larger bite angle and larger C^{Ph}–P–Cr angle, which offers an explanation for the poor selectivity and poor activity when using the PCP ligand in Cr-catalyzed ethylene oligomerization.[9,16]

Several studies have reported that the catalytic activity and selectivity for ethylene oligomerization were strongly influenced by the reaction conditions, such as temperature, ethylene pressure, Al/Cr ratio, etc. In an attempt to improve the catalyst performance, precatalysts **1**, **4**, and **5** were selected for further investigation under different reaction conditions. The precatalysts were first tested under various reaction temperature and ethylene pressure, and the results are shown in Table 2. For **1**, **4**, and **5**, increasing temperature from 40 to 60 °C leads to an increase in activity and 1-hexene selectivity. A decrease in the formation of undesirable cyclic C6 products was observed and thus led to an increase in selectivity to 1-hexene within the C6 fraction (Table 2, entries 1, 2, and 4). At 40 bar ethylene and at 60 °C, **5** achieved very high activity of up to 3869 kg/(g Cr/h) with 53.2% 1-hexene selectivity and an increased selectivity (93.4%) to 1-hexene within the C6 fraction, while selectivity toward 1-octene drops to 25.8% (Table 2, entry 4). For **5**, further increasing reaction temperature to 80 °C slightly decreased activity and the total selectivity toward 1-hexene and 1-octene and increased the formation of PE (Table 2, entry 5). **5** achieved high activity of 1324 kg/(g Cr/h) with the highest 1-hexene selectivity of 55.2% at low ethylene pressure of 20 bar under 80 °C (Table 2, entry 7). For **4**, decreasing ethylene pressure from 40 to 30 bar causes a dramatic decrease in activity, while **5** remained highly active at 30 bar similar to that at 40 bar (Table 2, entries 3 and 6).

The effect of Al/Cr molar ratio on catalytic properties and selectivity were investigated next, and the results are shown in Table 3. For **1**, **4**, and **5**, increasing the Al/Cr molar ratio from 500 to 700 enhanced the activities and produced more 1-hexene at the expense of 1-octene (Table 3, entries 1, 2, and 3). An extremely high activity of 4238 kg/(g Cr/h) was obtained using **5** with a high total selectivity of 79.1% toward valuable 1-hexene (46.0%) and 1-octene (33.1%) (Table 3, entry 3). Lowering the amount of MMAO-3A to 300 equiv led to a decrease in the activity for **5** and produced more PE (Table 3, entry 4).

CONCLUSIONS

Novel Cr(III) complexes with carbon-bridged diphosphine ligands of the types $\{Ph_2PCH(R)CH_2PPh_2\}$ and $\{Ph_2PC(R)=CHPPh_2\}$ have been prepared, which upon activation with MMAO-3A, are highly active for ethylene tri/tetramerization with considerable selectivity. We have presented that the ligand backbone substitution and bridge unsaturation play an

Table 2. Evaluation of 1, 4, and 5/MMAO-3A for Selective Oligomerization under Different Reaction Conditions[a]

				oligomer distribution (wt %)						
entry (cat.)	C_2H_4 pressure (bar)	T (°C)	activity (kg/g Cr/h)	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]	PE (wt %)[c]
1 (**1**)	40	60	1100	25.2	75.8	7.9	54.4	99.4	11.3	6.4
2 (**4**)[d]	40	60	2694	35.0	77.1	10.4	42.8	99.2	13.5	1.0
3 (**4**)	30	40	920	19.2	53.8	16.2	52.9	98.3	9.5	0.8
4 (**5**)[d]	40	60	3869	53.2	91.3	4.8	25.8	99.0	15.4	3.4
5 (**5**)[d]	40	80	3227	49.7	93.4	2.9	17.5	98.0	28.3	9.8
6 (**5**)	30	40	2188	41.6	84.5	7.4	35	99.3	15.7	1.0
7 (**5**)	20	80	1324	55.2	92.5	3.9	19.4	98.3	20.3	0.8

[a]Conditions: 120 mL reactor, 1.0 μmol of precatalyst, 500 equiv. of MMAO-3A, 30 mL of methylcyclohexane, 30 min. [b]wt % of liquid products (oligomers). [c]wt % of total product (oligomers + polymer). [d]15 min.

dx.doi.org/10.1021/cs400651h | ACS Catal. 2013, 3, 2311–2317

Table 3. Evaluation of the Effect of Co-Catalyst on Selective Oligomerization[a]

entry (cat.)	MMAO-3A (equiv)	activity (kg/g Cr/h)	oligomer distribution (wt %) 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]	PE (wt %)[c]
1 (**1**)	700	1542	27.9	77.3	8.0	54.1	99.3	9.1	1.5
2 (**4**)	700	3223	31.2	73.5	11.3	43.3	99.2	13.4	0.6
3 (**5**)	700	4238	46.0	87.6	6.4	33.1	99.3	13.5	0.3
4 (**5**)[d]	300	1711	43.3	85.7	7.1	34.5	99.2	14.4	6.8

[a]Conditions: 120 mL of reactor, 1.0 μmol of precatalyst, MMAO-3A, 40 bar of ethylene, 30 mL of methylcyclohexane, 40 °C, 15 min. [b]wt % of liquid products (oligomers). [c]wt % of total product (oligomers + polymer). [d]30 min.

important role in determining the activity and selectivity of these ethylene oligomerization catalytic systems. Introduction of a bulky group on the backbone in diphosphine ligand with unsaturated linker dramatically increases the activity and favors the formation of 1-hexene. The Cr complexes bearing diphosphine ligand with an unsaturated linker achieved extremely high activities, which are higher than those bearing diphosphine ligand with a saturated linker. The highest selectivity of 64.7% toward 1-octene was achieved using diphosphine ligand with a methyl-substituted saturated linker, and the highest activity of 4238 kg/(g Cr/h) was obtained using diphosphine ligand $\mathbf{L^5}$ with a tert-butyl-substituted unsaturated linker. The selectivity to 1-hexene can be improved up to 55.2% using $\mathbf{L^5}$ at 20 bar and 80 °C. X-ray single-crystal crystallographic analysis shows, although Cr complex **11** bearing $\mathbf{L^5}$ has a larger bite angle than that bearing a typical PNP ligand, a smaller C^{Ph}−P−Cr angle is observed in it. The feature could offer an explanation to the very high activity and good total selectivity toward valuable 1-hexene and 1-octene achieved by complex **5**.

With the fine-tuned ligand backbone, such backbone-substituent of carbon-bridged diphosphine ligand system would allow for extensive ligand variation by further modifying the backbone-substituents on the two backbone-carbon atoms and the phosphine substituents and thus probably offer a mode for precise understanding of the impact of ligand variations on catalytic performance. Ongoing experiments are directed at the development of other phosphine ligand systems especially on the use of carbon-bridged diphosphine ligands to support olefin oligomerization.

EXPERIMENTAL SECTION

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 $CDCl_3$: 100.0 ppm). X-ray diffraction analysis was performed by using a Bruker Smart-1000 X-ray diffractometer. Elemental analyses were performed by the microanalytical laboratory in house. 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. Diphosphine ligands $\mathbf{L^1}$ and $\mathbf{L^2}$ were prepared according to modified literature method,[13] and their spectra were consistent with that of the published data.[17,18] $\mathbf{L^3}$ and $\mathbf{L^5}$ were prepared according to the literature method,[14] and their spectra were consistent with that of the published data.[14]

Preparation and Characterization. *Synthesis of Diphosphine Ligand L^1, {$Ph_2PCH(Me)CH_2PPh_2$}.* 1,2-Propanediol (1.0 g, 13.2 mmol) and NEt_3 (4.0 mL, 28.9 mmol) was dissolved in CH_2Cl_2 (50 mL), and then methanesulfonyl chloride (2.15 mL, 27.6 mmol) was added dropwise. After 20 min, the mixture was warmed to room temperature and stirred overnight. After full consumption of the reagents, water was added, and the mixture was extracted with CH_2Cl_2; the combined organic layers were washed with brine and dried with anhydrous Na_2SO_4. Evaporating the solvent afforded the crude MeCH(OMs)-CH_2(OMs), which was used without characterization. MeCH-(OMs)CH_2(OMs) was dissolved in THF (30 mL); the solution was cooled to −78 °C, and a THF solution of $LiPPh_2$, prepared from ^{n}BuLi (1.6 M, 16.4 mL, 26.3 mmol) and $HPPh_2$ (4.8 g, 26.3 mmol), was added dropwise. After 20 min, the mixture was warmed to room temperature and stirred overnight. The solvent was removed under vacuum, and water was added to give a white solid. The solid was filtered and then purified by chromatography on short silica gel to yield $\mathbf{L^1}$ (3.1 g, 57.2%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41−7.21 (m, 20H), 2.31−2.26(m, 2H), 1.90−1.81 (m, 1H), 1.28 (dd, 3H).

Synthesis of Diphosphine Ligand L^2, {$Ph_2PCH(Ph)$-CH_2PPh_2}. The ligand $\mathbf{L^2}$ was prepared via a similar procedure, in yield of 61.7%, illustrated below for $\mathbf{L^1}$. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38−6.81 (m, 25H), 3.34−3.27 (m, 1H), 2.58−2.43 (m, 2H).

Synthesis of Diphosphine Ligand L^4, {$Ph_2PC(Cy)$=$CHPPh_2$}. Carbon-bridged diphosphine ligand $\mathbf{L^4}$ was prepared in yield of 51.8%, according to literature method[14] starting from commerially available cyclohexylethyne. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23−7.37 (m, 20H), 7.03 (d, J = 36 Hz, 1H), 2.08−2.02 (m, 1H), 1.49−1.52 (m, 2H), 1.35−1.38 (m, 2H), 1.23−1.31 (m, 2H), 1.13−1.19 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.21, 161.05, 161.02, 160.09, 141.01, 140.94, 140.71, 140.65, 139.98, 139.96, 139.90, 139.87, 136.63, 136.59, 136.53, 136.48, 133.52, 133.36, 133.12, 132.91, 132.76, 132.58, 132.13, 128.31, 128.27, 128.22, 128.13, 128.10, 44.05, 26.59, 26.41, 25.97. ^{31}P NMR ($CDCl_3$): δ = −4.08 (dd, J_1 = 34.9 Hz, J_2 = 166.4 Hz); −25.83 (d, J = 166.4 Hz).

*Synthesis of Complexes **1**−**5**. [L^1$CrCl_2$(μ-Cl)]$_2$ (**1**).* To a solution of $Ph_2PCH(Me)CH_2PPh_2$ $\mathbf{L^1}$ (0.123 g, 0.30 mmol) in dry CH_2Cl_2 (3 mL) was added [$CrCl_3(THF)_3$] (0.105 g, 0.28 mmol), and the resulting mixture was stirred at room temperature for 8 h. The solvent was evaporated, and 10 mL of *n*-hexane was added to complete precipitation. The product was collected by filtration, washed with 10 mL of *n*-hexane, and dried in vacuo, yielding **1** (0.146 g, 92.1%) as blue powders.

dx.doi.org/10.1021/cs400651h | ACS Catal. 2013, 3, 2311−2317

Anal. Calcd for $C_{54}H_{52}Cl_6Cr_2P_4$ (%): C, 56.81; H, 4.59. Found: C, 57.02; H, 4.25.

*$[L^2CrCl_2(\mu\text{-}Cl)]_2$ (**2**).* The complex **2** was prepared as blue powder via a similar procedure, in yield of 93.0%, illustrated below for **1**. Anal. Calcd for $C_{64}H_{56}C_{16}Cr_2P_4$ (%): C, 60.73; H, 4.46. Found: C, 60.61; H, 4.53.

*$[L^3CrCl_2(\mu\text{-}Cl)]_2$ (**3**).* To a solution of $Ph_2PC(Ph)=CHPPh_2$ L^3 (0.141 g, 0.30 mmol) in dry toluene (10 mL) was added $[CrCl_3(THF)_3]$ (0.105 g, 0.28 mmol). The resulting mixture was stirred at 80 °C for 8 h, and a blue precipitate formed. The product was collected by filtration, washed with 10 mL of *n*-hexene, and dried in vacuo, yielding **3** (0.168 g, 95.3%) as blue powder. Anal. Calcd for $C_{64}H_{52}Cl_6Cr_2P_4$ (%): C, 60.92; H, 4.15. Found: C, 60.39; H, 4.67.

*$[L^4CrCl_2(\mu\text{-}Cl)]_2$ (**4**).* The complex **4** was prepared as blue powder via a similar procedure, in yield of 96.1%, illustrated below for **3**. Anal. Calcd for $C_{64}H_{64}Cl_6Cr_2P_4$ (%): C, 60.35; H, 5.06. Found: C, 60.76; H, 5.39.

*$[L^5CrCl_2(\mu\text{-}Cl)]_2$ (**5**).* The complex **5** was prepared as blue powders via a similar procedure, in yield of 91.2%, illustrated below for **3**. Anal. Calcd for $C_{60}H_{60}C_{16}Cr_2P_4$ (%): C, 58.99; H, 4.95. Found: C, 59.27; H, 5.21.

*Synthesis of Complex **11**. $L^5Cr(CO)_4$ (**11**).* To a solution of L^5 (0.100 g, 0.220 mmol) in dry toluene (5 mL) was added $[Cr(CO)_6]$ (0.064 g, 0.29 mmol), and the resulting mixture was stirred under reflux for 48 h. The solvent was evaporated, and the residue was extracted into DCM (1 mL). Six mL of methanol was added to complete precipitation. The product was collected by filtration, washed with 10 mL of methanol, and dried in vacuo, yielding **11** (0.071 g, 52.0%) as white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (dd, J = 56.4, 4.4, 1H), 7.65 (t, J = 8.2 Hz, 4H), 7.53 (t, J = 8.2 Hz, 4H), 7.42−7.39 (m, 12H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.36, 146.99, 146.91, 146.53, 137.87, 137.85, 137.51, 137.49, 135.53, 135.50, 135.21, 135.17, 131.57, 131.47, 131.26, 131.15, 129.66, 129.56, 128.72, 128.62, 128.31, 128.21, 40.94, 40.81, 32.95. ^{31}P NMR ($CDCl_3$): δ = 98.90, 73.18. Anal. Calcd for $C_{34}H_{30}CrO_4P_2$ (%): C, 66.23; H, 4.90. Found: C, 66.36; H, 4.71.

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 cocatalysts (MMAO-3A) were combined in a Schlenk vessel in the ratios indicated in Tables 1−3. 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 closing the ethylene feed, cooling the system to 0 °C, depressurizing, and quenching 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 analyzed 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.

■ ASSOCIATED CONTENT

Supporting Information

Representative NMR spectra and crystallographic data (CIF) for **11**. 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.

■ ACKNOWLEDGMENTS

Financial support from Shanghai Pujiang Talent Program (11PJ1402500), the Fundamental Research Funds for the Central Universities (WK1114014), and the National Natural Science Foundation of China (21171056) is greatly acknowledged.

■ REFERENCES

(1) (a) McGuinness, D. S. *Chem. Rev.* **2011**, *111*, 2321. (b) Dixon, J. T.; Green, M. J.; Hess, F. M.; Morgan, D. H. *J. Organomet. Chem.* **2004**, *689*, 3641. (c) Wass, D. F. *Dalton Trans.* **2007**, 816. (d) Agapie, T. *Coord. Chem. Rev.* **2011**, *255*, 861.

(2) Manyik, R. M.; Walker, W. E.; Wilson, T. P. *J. Catal.* **1977**, *47*, 197.

(3) (a) Reagan, W. K. Phillips Petroleum Company, EP, 0 417 477, 1991. (b) Freeman, J. W.; Buster, J. L.; Knudsen, R. D. Phillips Petroleum Company, US Pat., 5856257, 1999. (c) Carter, A.; Cohen, S. A.; Cooley, N. A.; Murphy, A.; Scutt, J.; Wass, D. F. *Chem. Commun.* **2002**, 858. (d) McGuinness, D. S.; Wasserscheid, P.; Keim, W.; Hu, C.; Englert, U.; Dixon, J. T.; Grove, C. *Chem. Commun.* **2003**, 334. (e) McGuinness, D. S.; Wasserscheid, P.; Keim, W.; Morgan, D.; Dixon, J. T.; Bollmann, A.; Maumela, H.; Hess, F.; Englert, U. *J. Am. Chem. Soc.* **2003**, *125*, 5272. (f) Yu, Z.; Houk, K. N. *Angew. Chem., Int. Ed.* **2003**, *42*, 808. (g) Agapie, T.; Schofer, S. L.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2004**, *126*, 1304. (h) Rensburg, W. J.; Grove, C.; Steynberg, J. P.; Stark, K. B.; Huyser, J. J.; Steynberg, P. J. *Organometallics* **2004**, *23*, 1207. (i) McGuinness, D. S.; Wasserscheid, P.; Morgan, D. H.; Dixon, J. T. *Organometallics* **2005**, *24*, 552. (j) Bluhm, M. E.; Walter, O.; Döring, M. *J. Organomet. Chem.* **2005**, *690*, 713. (k) Nenu, C. N.; Weckhuysen, B. M. *Chem. Commun.* **2005**, 1865. (l) Elowe, P. R.; McCann, C.; Pringle, P. G.; Spitzmesser, S. K.; Bercaw, J. E. *Organometallics* **2006**, *25*, 5255. (m) Jabri, A.; Temple, C.; Crewdson, P.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *J. Am. Chem. Soc.* **2006**, *128*, 9238. (n) Agapie, T.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2007**, *129*, 14281. (o) McGuinness, D. S.; Suttil, J. A.; Gardiner, M. G.; Davies, N. W. *Organometallics* **2008**, *27*, 4238. (p) Jabri, A.; Mason, C. B.; Sim, Y.; Gambarotta, S.; Burchell, T. J.; Duchateau, R. *Angew. Chem., Int. Ed.* **2008**, *47*, 9717. (q) Vidyaratne, I.; Nikiforov, G. B.; Gorelsky, S. I.; Gambarotta, S.; Duchateau, R. *Angew. Chem., Int. Ed.* **2009**, *48*, 6552.

(4) (a) Zhang, J.; Braunstein, P.; Hor, T. S. A. *Organometallics* **2008**, *27*, 4277. (b) Zhang, J.; Li, A.; Hor, T. S. A. *Organometallics* **2009**, *28*, 2935. (c) Zhang, J.; Li, A.; Hor, T. S. A. *Dalton Trans.* **2009**, 9327.

(5) Klemps, C.; Payet, E.; Magna, L.; Saussine, L.; Le Goff, X. F.; Le Floch, P. *Chem.−Eur. J.* **2009**, *15*, 8259.

(6) Sydora, O. L.; Jones, T. C.; Small, B. L.; Nett, A. J.; Fischer, A. A.; Carney, M. J. *ACS Catal.* **2012**, *2*, 2452.

(7) Bollmann, A.; Blann, K.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; McGuinness, D. S.; Morgan, D. H.; Neveling, A.; Otto, S.; Overett, M. J.; Slawin, A. M. Z.; Wasserscheid, P.; Kuhlmann, S. *J. Am. Chem. Soc.* **2004**, *126*, 14712.

(8) (a) Blann, K.; Bollmann, A.; Dixon, J. T.; Hess, F.; Killian, E.; Maumela, H.; Morgan, D. H.; Neveling, A.; Otto, S.; Overett, M. J. *Chem. Commun.* **2005**, 622. (b) Blann, K.; Bollmann, A.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; Morgan, D. H.; Neveling, A.; Otto, S.; Overett, M. J. *Chem. Commun.* **2005**, 620. (c) Blann, K.; Bollmann, A.; de Bod, H.; Dixon, J. T.; Killian, E.; Nongodlwana, P.; Maumela, M. C.; Maumela, H.; McConnell, A. E.; Morgan, D. H.; Overett, M. J.; Pretorius, M.; Kuhlmann, S.; Wasserscheid, P. *J. Catal.* **2007**, *249*, 244. (d) Kuhlmann, S.; Blann, K.; Bollmann, A.; Dixon, J.

T.; Killian, E.; Maumela, M. C.; Maumela, H.; Morgan, D. H.; Prétorius, M.; Taccardi, N.; Wasserscheid, P. *J. Catal.* **2007**, *245*, 279.
(9) Overett, M. J.; Blann, K.; Bollmann, A.; de Villiers, R.; Dixon, J. T.; Killian, E.; Maumela, M. C.; Maumela, H.; McGuinness, D. S.; Morgan, D. H.; Rucklidge, A.; Slawin, A. M. Z. *J. Mol. Catal. A: Chem.* **2008**, *283*, 114.
(10) Kim, S. K.; Kim, T. J.; Chung, J. H.; Hahn, T. K.; Chae, S. S.; Lee, H. S.; Cheong, M.; Kang, S. O. *Organometallics* **2010**, *29*, 5805.
(11) (a) Dulai, A.; McMullin, C. L.; Tenza, K.; Wass, D. F. *Organometallics* **2011**, *30*, 935. (b) Licciulli, S.; Thapa, I.; Albahily, K.; Korobkov, I.; Gambarotta, S.; Duchateau, R.; Chevalier, R.; Schuhen, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 9225. (c) Shaikh, Y.; Gurnham, J.; Albahily, K.; Gambarotta, S.; Korobkov, I. *Organometallics* **2012**, *31*, 7427. (d) Shaikh, Y.; Albahily, K.; Sutcliffe, M.; Fomitcheva, V.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *Angew. Chem., Int. Ed.* **2012**, *51*, 1366.
(12) Zhang, J.; Teo, P.; Pattacini, R.; Kermagoret, A.; Welter, R.; Rogez, G.; Hor, T. S. A.; Braunstein, P. *Angew. Chem., Int. Ed.* **2010**, *49*, 4443.
(13) Bianchini, C.; Lee, H. M.; Meli, A.; Oberhauser, W.; Peruzzini, M.; Vizza, F. *Organometallics* **2002**, *21*, 16.
(14) Kondoh, A.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2007**, *129*, 4099.
(15) Rucklidge, A. J.; McGuinness, D. S.; Tooze, R. P.; Slawin, A. M. Z.; Pelletier, J. D. A.; Hanton, M. J.; Webb, P. B. *Organometallics* **2007**, *26*, 2782.
(16) Dulai, A.; de Bod, H.; Hanton, M. J.; Smith, D. M.; Downing, S.; Mansell, S. M.; Wass, D. F. *Organometallics* **2009**, *28*, 4613.
(17) Yeo, W. C.; Tee, S. Y.; Tan, H. B.; Tan, G. K.; Koh, L. L.; Leung, P. H. *Inorg. Chem.* **2004**, *43*, 8102.
(18) Zhang, Y.; Tang, L.; Pullarkat, S. A.; Liu, F.; Li, Y.; Leung, P. H. *J. Organomet. Chem.* **2009**, *694*, 3500.