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ACS Catal., **Just Accepted Manuscript** • DOI: 10.1021/cs4004968 • Publication Date (Web): 03 Sep 2013

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Selective ethylene tri-/tetramerization by *in situ* formed chromium catalysts stabilized by N, P-based ancillary ligand systems

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ABSTRACT: A series of N, P-based ancillary ligands have been synthesized and the corresponding catalysts, formed *in situ* by mixing one of the N, P-ligands, $Cr(acac)_3$ and MAO, have been tested for ethylene oligomerization. Under standard ethylene oligomerization conditions (30 bar of ethylene, 60 °C, methylcyclohexane as solvent), all the *in situ* formed complexes show catalytic activity producing oligomers together with varying amounts of polyethylene. Of all these combinations only the catalyst formed by mixing N-pyrrolyldiphenylphosphine with $Cr(acac)_3$ and MAO is capable of *selectively* oligomerizing ethylene, producing a mixture of 1-hexene and 1-octene in varying ratios alongside a small amount of PE. Further investigations on this catalyst system reveal that the presence of a small volume-% of toluene favors the production of 1-octene. However, in pure toluene as solvent the selectivity towards 1-hexene/1-octene is lost and a statistic mixture of α-olefins is produced. Moreover, the choice of the co-catalyst is found to dramatically influence the composition of the liquid products. By careful adjustment of the reaction conditions (temperature, ethylene pressure, catalyst loading and ligand/Cr ratio), the 1-hexene/1-octene molar ratio can be tuned from 0.3 to 20 and a selectivity of 1-octene formation can be achieved up to 74 %.

KEYWORDS: selective ethylene oligomerization, ethylene tetramerization, chromium catalyst, ligand design, solvent effect, DFT calculation

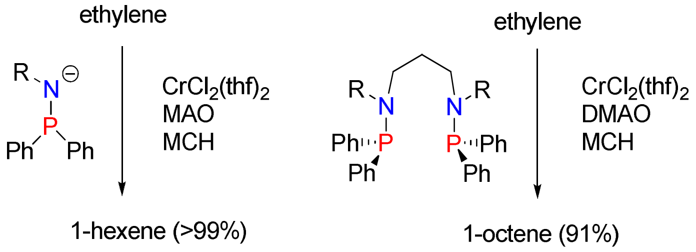
Introduction

As important comonomers for the production of linear low density polyethylene, 1-hexene and 1-octene are two highly desired linear α-olefins. To collect these light fractions from a broad distribution of oligomers, typically obtained by the conventional non-selective oligomerization processes, requires an economically unfavorable separation step. Selective production of 1-hexene and 1-octene directly by selective ethylene tri- or tetramerization is therefore highly desired and has stimulated both academic and industrial research.

Among all the transition metal-based catalysts, chromium catalysts have proven to be the most promising candidates for selective ethylene oligomerization.[1-3] Typical examples are the Chevron-Phillips trimerization catalyst,[4] the first and sole trimerization system to be successfully commercialized, and the few existing tetramerization systems with 1-octene selectivities in the range of 70 %.[5-6] On the other hand, the variety of oxidation states and spin states known for chromium severely complicate mechanistic studies of these catalysts.[7-23] As a consequence, despite the successful developments of numerous chromium-based selective ethylene trimerization and tetramerization systems, the nature of the active species is still not fully understood although there are strong arguments for a Cr(I)/Cr(III) redox couple.[8-10,15,17-18,24-35]

Besides the choice of the metal center, the desired catalytic selectivity can be tuned by designing ancillary ligands with the desired structural and electronic properties to assist the generation and stabilization of active species for selective ethylene oligomerization. Since the discovery of the chromium bis(diphenylphosphino)amine systems, which are adaptable to facilitate either ethylene trimerization[36] or tetramerization,[5] the family of N, P-based ligands eligible for selective ethylene oligomerization has gradually been expanded.[37-46] Recent studies on chromium catalysts stabilized by monoanionic N, P-based ligands[41] showed the capability of producing pure 1-hexene (> 99 %) along with small quantities of polyethylene (PE). This system could be tuned towards ethylene tetramerization[38] (producing 91 % of 1-octene with 1-hexene as the only oligomeric by-product) by assembling two N, P-based units with a propylenic bridge (Scheme 1).

Herein we describe the development of a new series of N, P-based ligands by replacing the dialkyl amine groups in the ligands mentioned above with nitrogen-containing heterocycles. The catalysts, formed *in situ* by mixing different combinations of ancillary ligands, chromium precursors and co-catalysts, were systematically tested under varied reaction conditions.



Scheme 1. Chromium aminodiphenylphosphine systems for ethylene trimerization and tetramerization.

Results and discussion

All the N, P-based ligands used in this study (Figure 1) were synthesized in a two-step process. The nitrogen-contained heterocyclic compounds were first deprotonated by triethylamine or n-butyllithium. Then chlorodiphenylphosphine or dichlorophenylphosphine was added dropwise to form the title compounds via salt elimination.

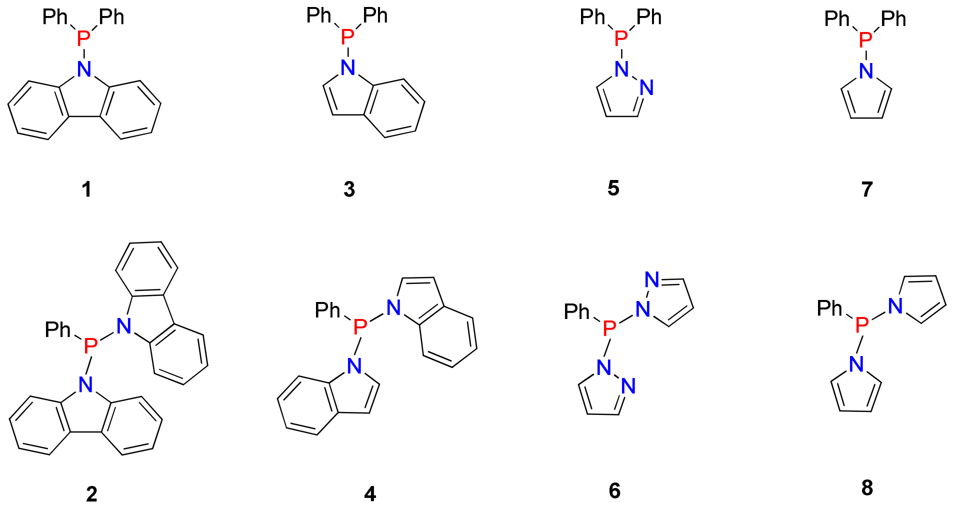


Figure 1. Illustration of the series of N, P-based ancillary ligands used in this study.

A major advantage of chromium-based selective ethylene oligomerization catalysts stabilized by neutral ancillary ligands is that they can effectively be generated *in situ* by mixing the ancillary ligand with an appropriate chromium precursor and the activator (*i.e.* MAO).[47] This simple catalyst preparation process significantly speeds up preliminary screening studies. In this study the N, P ancillary ligands (Figure 1) were mixed with Cr(acac)$_3$ in dry methylcyclohexane and stirred for at least four hours at room temperature before each run. Under typical ethylene oligomerization conditions (Table 1), upon activation with MAO (10 wt% in toluene) all the *in situ* formed Cr species showed catalytic activity. An instant temperature jump after the injection of catalyst was observed in all the cases, and after 10 to 15 minutes the temperature started to decrease gradually. The observed activities are moderate, which is most likely to be the result of the poor solubility of the catalysts in methylcyclohexane, and/or due to the insufficient separation of Cr cations and counterions in the highly apolar medium.[48] Alternatively, the catalysts themseleves might simply be not that reactive towards ethylene coordination and insertion. All catalysts, except the one obtained using ligand **7**, produced a statistic mixture of α-olefins and varying amounts of PE. Under the conditions applied (methylcyclohexane as solvent, 60 °C, 30 bar of ethylene), the catalyst based on ligand **7** produced a mixture of 1-hexene (56 %) and 1-octene (40 %) and only small amounts of higher olefins (4 %) along with a minor amount of PE (8 wt%). For most runs, the amount of PE obtained is too high to be part of the statistic product distribution, which suggests that besides the oligomerization catalyst also an independent polymerization catalyst exists in the system.

Table 1. Catalytic tests using the mixture of $Cr(acac)_3$ and N, P-based ligands activated by MAO.

Ligand	PE	PE	LAO	Activity	$C_6^=$	$C_8^=$
	(g)	(wt%)	(g)	(g/mmol Cr/h)	(mol%)	
1	0.51	60	0.34	57	24.3	24.6
2	0.79	14	4.83	375	42.0	29.3
3	0.52	42	0.71	82	15.3	32.7
4	0.44	37	0.74	79	35.1	24.0
5	0.72	53	0.64	91	37.9	28.2
6	1.00	52	0.93	129	38.2	29.7
7	0.45	8	4.69	361	39.5	56.4
8	0.44	34	0.85	86	38.6	24.0
-	1.82	100	-	122	-	-

Conditions: 30 μmol of $Cr(acac)_3$ and ligand, 500 equivalents of MAO, methylcyclohexane as solvent (100 mL total volume), 60 °C, 30 bar of ethylene, 30 minutes.

Given the closely-related structure of the diphenylphosphine ligands **1**, **3**, **5** and **7**, it is confusing that exclusively the chromium complex stabilized by ligand **7** gave selectivities towards 1-hexene and 1-octene. Attempts to obtain insights into the connectivity of the chromium complexes by isolating single crystals suitable for X-ray diffraction analysis, unfortunately turned out to be unsuccessful. All the crystals grown from the solutions of the chromium complexes were identified to be the initial reactant chromium precursors (*i.e.* $CrCl_3(THF)_3$), which is a indication of the weak binding strength between the ligands and the chromium center in the neutral, non-activated species. The easy loss of the ancillary ligand also raises the possibility that the PE formed in the present system might partially arise from a ligand-free chromium species. This assumption is supported by the fact that upon activation with MAO, $Cr(acac)_3$ itself enables ethylene polymerization albeit with low activity (Table 1).

Despite the uncertain features that endow Cr/**7** the ability to promote ethylene tri- and tetramerization, its promising catalytic performances encouraged us to further investigate the Cr/**7** system under various reaction conditions.

First the effect of different chromium precursors on the catalytic behavior was investigated (Table 2). Despite the varying activities, systems using $CrCl_3(THF)_3$, $Cr(acac)_3$ or $Cr(EH)_3$ (acac = acetylacetonate, EH = 2-ethyl-hexanoate) as chromium sources showed similar selectivities towards 1-hexene and 1-octene, which indicates that the same active species for selective ethylene tri- and tetramerization is formed regardless the chromium precursor used. In the case of $CrCl_2(THF)_2$, more C16 and C20 products were detected. Probably, these two higher oligomers are the secondary products of co-trimerization or co-tetramerization of ethylene, 1-

hexene or 1-octene. The formation of C17 products from a co-oligomerization of ethylene and 1-pentene has proved that $CrCl_2(THF)_2$/**7** is capable of incoporating α-olefins, although it is unclear that these C17 products arise from the combination of 1-pentene with which α-olefins (possible combinations: C5+C8+C2+C2, C5+C5+C5+C2, C6+C6+C5, etc.) Chlorine-free precursors are favored since they afford higher activity and produce less PE. The enhanced activity probably resulted from a better solubility of $Cr(acac)_3$ and $Cr(EH)_3$ in methylcyclohexane.

Table 2. Catalytic tests using **7** combined with different chromium precursors.

Cr precursor	PE (g)	PE (wt%)	LAO (g)	Activity (g/mmol Cr/h)	$C_6^=$ (mol%)	$C_8^=$ (mol%)
$CrCl_3(THF)_3$	0.70	73	0.26	193	40.4	58.0
$CrCl_2(THF)_2$	0.38	72	0.15	106	23.8	51.4
$Cr(acac)_3$	0.29	11	2.40	538	37.0	58.3
$Cr(EH)_3$	0.66	17	3.22	775	37.2	56.6

Conditions: 10 µmol of $Cr(acac)_3$ and **7**, 500 equivalents of MAO, methylcyclohexane as solvent (100 mL total volume), 60 °C, 30 bar of ethylene, 30 minutes.

There are various occasions known where the presence of toluene poisons the selective ethylene oligomerization catalyst or converts it into a non-selective ethylene oligomerization catalyst.[8-9,26,37-38,41] Although direct proof is not available in the literature,[8-9,26,49-50] it is likely that

Cr(I)-arene complexes are formed. Hence, in an attempt to further improve the catalytic activity as well as the overall selectivity for 1-hexene and 1-octene formation, dried MAO (DMAO) was used as co-catalyst instead of a toluene solution of MAO. Indeed, the toluene-free system showed a doubling in activity, however, the selectivity simultaneously shifted from 1-octene to 1-hexene (Table 3, entry 2). The addition of extra trimethylaluminum (TMA) (10 %) to the DMAO did not restore the 1-octene selectivity.[35] In contrast, it led to a further increase of 1-hexene selectivity as well as activity (Table 3, entry 3). Interestingly, addition of 3.5 mL (33 mmol, the same volume as the MAO toluene solution) of toluene resulted in the original catalytic behavior obtained with MAO as co-catalyst (Table 3, entries 1 and 4). This finding indicates that for the current system a small amount of toluene plays a crucial role with respect to the selectivity for 1-octene versus 1-hexene. Using chlorobenzene or hexamethylbenzene instead of toluene demonstrated that using a less coordinating or a more polar arene has a beneficial effect on the catalytic activity, but also leads to a slight shift in selectivity towards 1-hexene (Table 3, entries 5, 7). There seems to be no straightforward interpretation for how the arenes affect 1-hexene and 1-octene selectivity. One possible explanation might be that arenes feature a hemilabile coordinative behavior during ethylene coordination and insertion, which thereby influences the kinetics of insertion versus β-H transfer of the chromacycloheptane intermediate. In this regard, toluene should be considered as a reagent to the chromium catalyst rather than a solvent simply increasing polarity. Considering the shift in selectivity requires a contribution from considerably large equivalents of toluene (*ca.* 3,300 equiv.), a relatively weak interaction between toluene and the chromium center is expected.

Table 3. The effect of different arenes on the catalytic behavior of Cr(acac)$_3$/**7**.

Entry	Co-catalyst	Arene	PE	LAO	Activity	$C_6^=$	$C_8^=$
#	(equiv.)	(mmol)	(g)	(g)	(g/mmol Cr/h)	(mol%)	
1	MAO (500)	toluene (33)	0.29	2.40	538	37.0	58.3
2	DMAO (500)	-	1.45	4.42	1174	67.4	30.9
3	DMAO (500) / TMA (50)	-	1.29	6.84	1626	79.8	18.8
4	DMAO (500)	toluene (33)	0.82	1.94	553	40.2	55.3
5	DMAO (500)	PhCl (33)	1.42	7.85	1853	71.0	28.4
6	DMAO (500)	toluene (5)	0.59	2.96	710	49.9	49.2
7	DMAO (500)	C_6Me_6 (5)	0.17	0.65	165	58.3	38.6

Conditions: 10 μmol of Cr(acac)$_3$ and **7**, methylcyclohexane as solvent (100 mL total volume), 60 °C, 30 bar of ethylene, 30 minutes.

A detailed investigation was further carried out to elucidate the influence of toluene on the selectivity for 1-hexene and 1-octene by carefully varying the amount of toluene added to the toluene-free system (Figure 2). It was found that introduction of 1-5 volume-% of toluene gradually shifts the dominant liquid fraction from 1-hexene to 1-octene, up to a maximum of 59 % of 1-octene (for 5 volume-% of toluene). Moreover, the addition of toluene had a strong influence on the catalytic activity as well. Just 2 volume-% of toluene proved to be enough to result in a three-fold drop of the original catalytic activity. Above 10 volume-% of toluene, non-selective ethylene oligomerization became more and more prominent with increasing toluene concentration. Using pure toluene as solvent resulted in a statistic distribution of oligomers with a minor enrichment in 1-hexene and 1-octene, indicating the co-existence of active species enabling selective and non-selective ethylene oligomerizations in the system. The activity of the non-selective catalyst was found to be comparable to that of the selective catalyst in the absence of toluene.

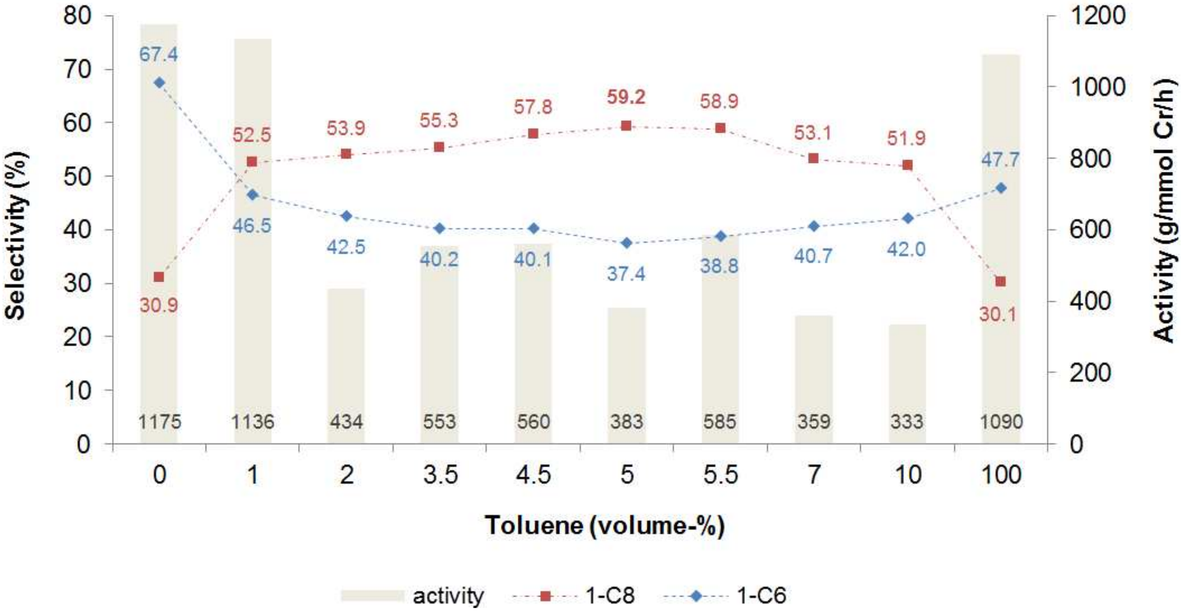


Figure 2. Influence of toluene concentration on activity and selectivity for 1-hexene and 1-octene. Dotted lines have no physical meanings. Conditions: 10 μmol of Cr(acac)$_3$ and **7**, 500 equivalents of DMAO, 60 °C, 30 bar of ethylene, 30 minutes, methylcyclohexane and/or toluene as solvent (100 mL total volume).

The influence of other reaction conditions on the catalytic behavior was subsequently investigated with Cr(acac)$_3$/**7** (Table 4). Besides the striking effect of toluene, the selectivity for 1-hexene and 1-octene as well as the catalytic activity were dramatically influenced by the choice of the co-catalyst. A recent study on the Sasol Cr-PNP system shed light on the role of the co-catalyst during catalysis, suggesting that the selectivity can be affected remarkably by the interaction strength between the chromium center and the aluminum species.[48] Using modified MAO (MMAO, 7 % Al in heptane solution) instead of MAO shifted the system to ethylene trimerization with 91 % 1-hexene selectivity (Table 4, entry 2). The combination of DMAO and triisobutylaluminum (TIBA) also promoted selective ethylene oligomerization, albeit with lower 1-hexene selectivity (80 %) and a significant amount of PE being formed (30 %; Table 4, entry 3). On the other hand, introduction of diethylaluminum chloride (DEAC) in combination with DMAO turned the system inactive (Table 4, entry 4). This observation is in contrast with the positive effect of DEAC on the Chevron-Phillips system,[47] in which the hemilabile interaction between chromium and the introduced chlorine from DEAC benefits the catalytic activity.[18] In the present study, addition of either chlorine-contained chromium precursors or chlorine-contained co-catalysts negetively affected the catalytic performance.

Besides the abovementioned strong influences, catalyst loading, ligand/Cr ratio, temperature and ethylene pressure had a minor effect but with clear trends on both catalytic activity and selectivity (Figure 3). Variation of catalyst loading from 5 μmol to 30 μmol (*i.e.* 0.05 mM and 0.3 mM) resulted in a gradual decline of 1-octene selectivity as well as catalytic activity (Table 4, entries 1, 8, 9, 10). The impact of catalyst loading might result from a shift in equilibria between different, for example mononuclear and binuclear,[7] active species. A dramatic effect of catalyst loading on selectivity has recently been reported for a chromium/PN ligand-based ethylene tetramerization system, in which increasing the catalyst loading from 15 μmol to 60 μmol (*i.e.* 0.15 mM and 0.6 mM) led to varied 1-hexene/1-octene ratios, and the highest 1-octene selectivity was achieved when 30 μmol of catalysts were employed.[38] Raising the ligand/Cr ratio from 1 to 3 resulted in a switch in selectivity from 1-octene towards 1-hexene, while the highest activity was achieved when 2 equivalents of ligands were employed (Table 4, entries 1, 11, 12).

The influence of the ligand/Cr ratio on the catalytic behavior might be attributed to a change in the coordination environment of chromium. Introduction of more ancillary ligands could give rise to a competitive coordination to the chromium center of a second ligand **7** on the expenses of toluene, thereby influencing the subsequent formation of active species responsible for selective oligomerization. As was also found for the Cr-PNP system,[51] lowering the reaction temperature was found to be beneficial for the 1-octene formation with a compromise in catalytic activity (Table 4, entries 1, 5). Finally, higher ethylene pressure was found to favor both 1-octene selectivity and catalytic activity (Table 4, entries 1, 6, 7). The positive effect of low temperature and high ethylene pressure on 1-octene formation can be attributed to the enhanced ethylene solubility in methylcyclohexane solution under these conditions.[52] This is in line with the reaction order in ethylene concentration for ethylene tetramerization being higher than that for ethylene trimerization, as was found to be the case for other selective ethylene trimerization/tetramerization systems.[5,53-57] By careful adjustment of the reaction conditions, an activity of ca. 2,000 g/mmol Cr/h could be reached with 57 % of 1-octene and 42 % of 1-hexene of the liquid fraction. Changing the reaction conditions for an optimum 1-octene selectivity (> 70 %) resulted in an aprox. 50 % reduction of the catalytic activity (Table 4, entries 7, 14).

Table 4. Catalytic tests using $Cr(acac)_3$/**7** as catalyst precursor under different conditions.[a]

Entry \#	Co-catalyst (equiv.)	PE (g)	PE (wt%)	LAO (g)	Activity (g/mmol Cr/h)	$C_6^{=}$ (mol%)	$C_8^{=}$
1	MAO (500)	0.29	11	2.40	538	37.0	58.3
2[b]	MMAO (500)	0.43	7	5.71	555	90.8	4.6
3[b]	DMAO(500) / TIBA(100)	3.59	30	3.65	347	79.9	12.5
4	DMAO(500) / DEAC(100)	-	-	-	-	-	-
5[c]	MAO (500)	0.57	28	1.48	409	29.2	66.1
6[d]	MAO (500)	0.33	23	1.10	286	36.4	60.9
7[e]	MAO (500)	0.61	9	5.97	1316	28.1	70.5
8[f]	MAO (500)	0.23	10	2.06	917	36.3	60.5
9[g]	MAO (500)	0.56	13	3.68	423	39.8	57.2
10[b]	MAO (500)	0.45	8	4.69	361	39.5	56.4
11[h]	MAO (500)	0.49	8	5.38	1174	45.3	52.9
12[i]	MAO (500)	0.97	21	3.63	921	47.8	47.2
13[e, h]	MAO (500)	0.46	4	10.31	2154	41.5	57.1
14[c, e]	MAO (500)	0.63	15	3.61	848	22.8	73.7
blank	MAO (500)	0.01	100	-	-	-	-

Conditions: [a]10 µmol of $Cr(acac)_3$ and **7**, methylcyclohexane as solvent (100 mL total volume), 60 °C, 30 bar of ethylene, 30 minutes. [b]30 µmol of $Cr(acac)_3$ and **7**. [c]40 °C. [d]20 bar of ethylene. [e]50 bar of ethylene. [f]5 µmol of $Cr(acac)_3$ and **7**. [g]20 µmol of $Cr(acac)_3$ and **7**. [h]10 µmol of $Cr(acac)_3$, 20 µmol of **7**. [i]10 µmol of $Cr(acac)_3$, 30 µmol of **7**.

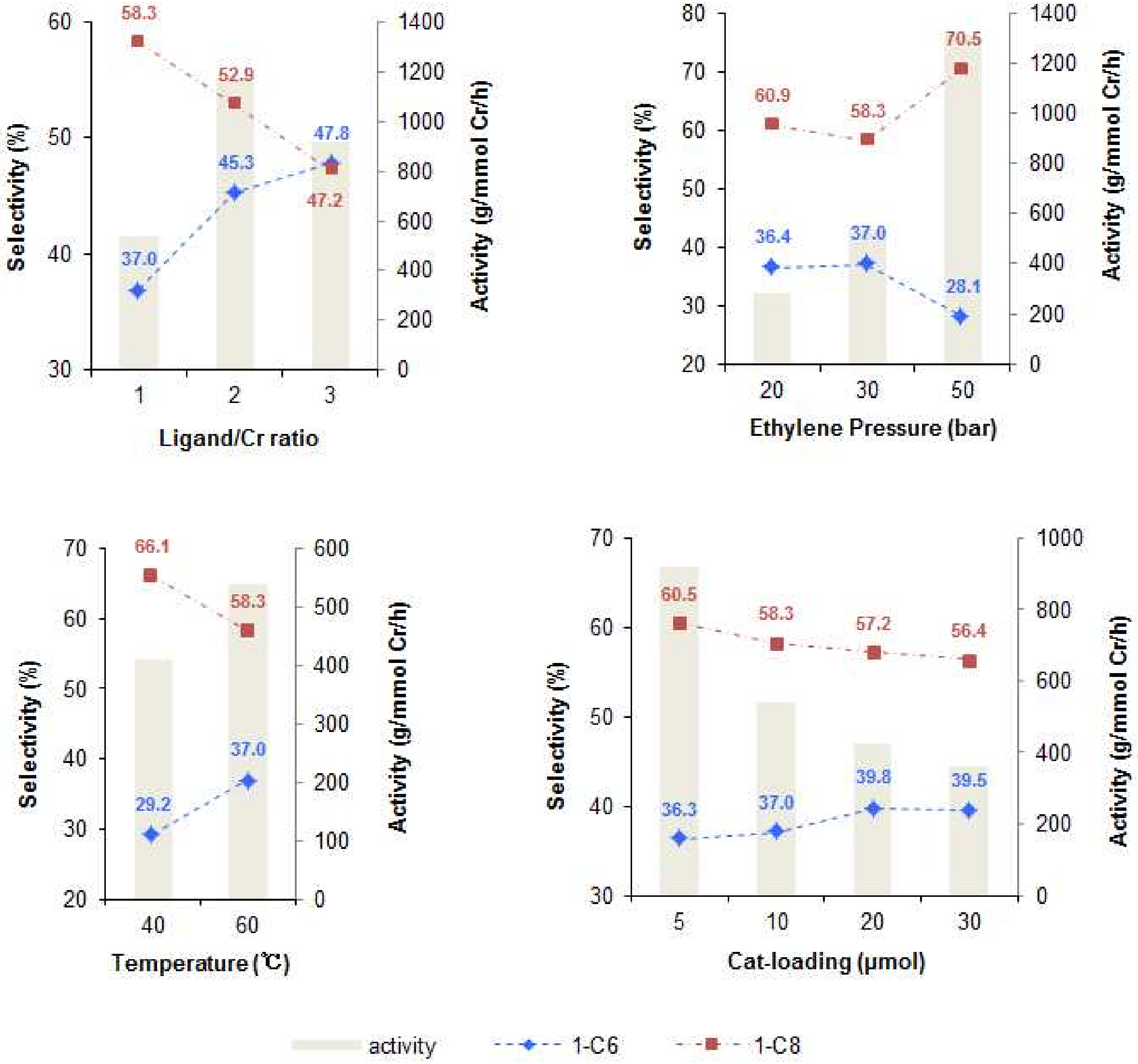
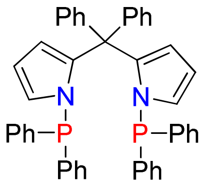


Figure 3. Influence of reaction conditions on activity and selectivity for 1-hexene and 1-octene. Dotted lines have no physical meanings. Conditions: 10 μmol of Cr(acac)$_3$ and **7**, 500 equivalents of MAO, 60 °C, 30 bar of ethylene, 30 minutes, methylcyclohexane as solvent (100 mL total volume). Adjustments of reaction conditions are shown in the figure.

Inspired by the works of Gambarotta and co-workers (Scheme 1),[38,41] endeavors were also made to achieve higher 1-octene selectivity by introducing ligands with double units of **7** linked by a carbon bridge (Figure 4). Upon activation with MAO in toluene, Cr(acac)$_3$/**9** produced a statistic distribution of oligomers with a minor enrichment in 1-hexene, while in methylcyclohexane the system shifted to ethylene polymerization. The fairly low catalytic activities shown in both solvents might have arised from the poor solubility of the catalysts. Therefore ligand **10**, assumed to have an improved solubility in methylcyclohexane, was synthesized. Cr(acac)$_3$/**10** indeed shows an improved productivity, however, the catalyst system still lacked distinct selectivity towards 1-hexene or 1-octene.



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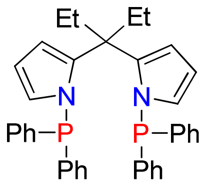

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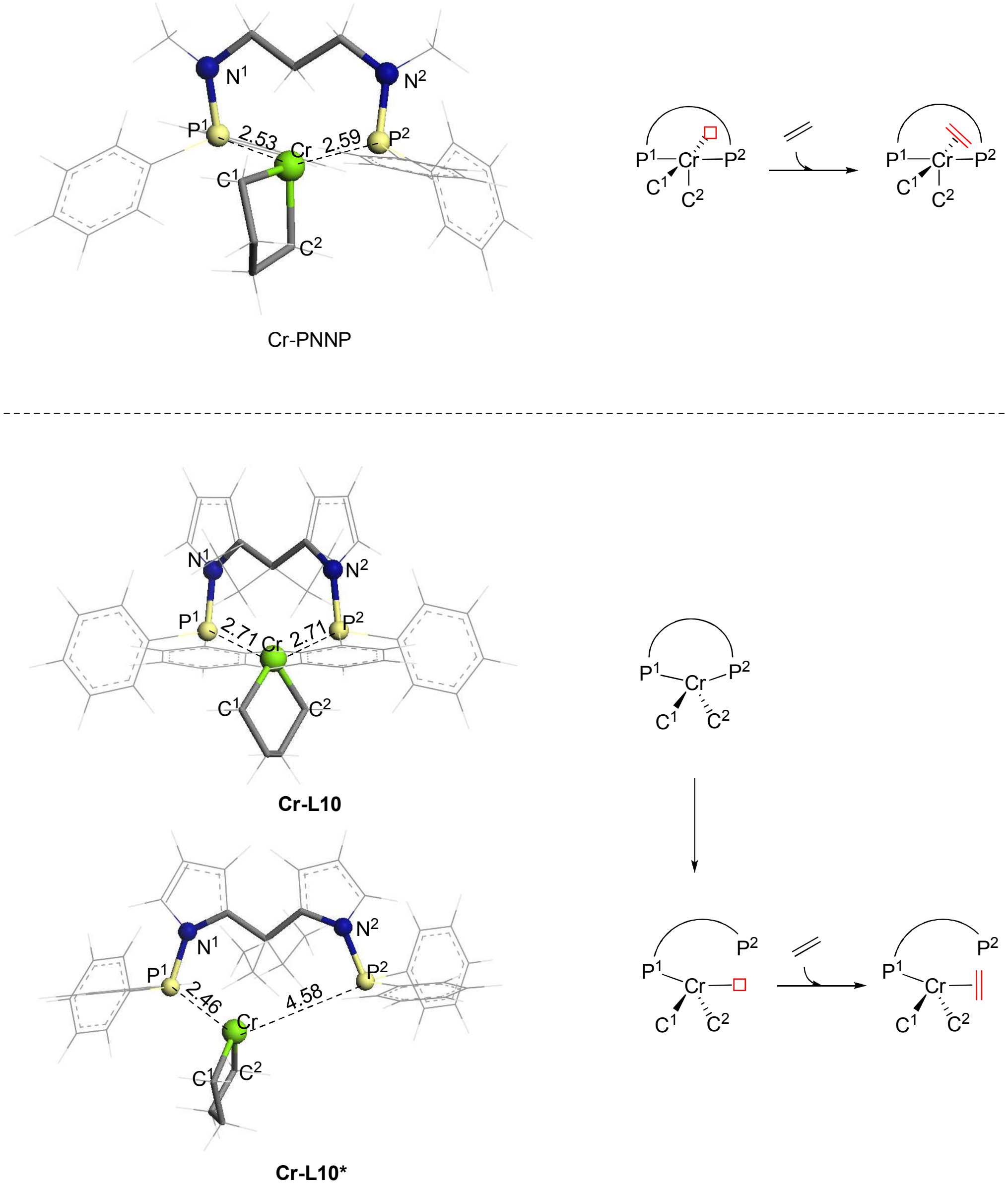
Figure 4. Illustration of N, P-based ligands with two units of **7** linked by a carbon bridge.



Scheme 2. Comparison of Cr/**10** complex (below) with a related chromacyclopentane containing the PNNP ligand published by Gambarotta.[38] Unit of Cr-P distance is Å.

Considering the fact that **10** has a similar backbone as the PNNP ligand developed by Gambarotta,[38] the quite different catalytic behavior from their corresponding chromium complexes was unexpected. To explore the possible reason for this distinguishable difference between the two systems, density functional theory (DFT) calculations were conducted on the corresponding chromacyclopentane species, which are important active intermediates in the hypothetical metallacycle mechanism[31-32,34,58] for selective ethylene oligomerization and are often found to be involved in the rate-determining step in the reaction cycle.[15,18-19,23] Interestingly, the complexes clearly exhibit different coordination geometries in the optimized chromacyclopentane structures. The complex containing the PNNP ligand synthesized by Gambarotta (Cr-PNNP) features an octahedral geometry, with a vacant site feasible for the coordination of the third ethylene. Conversely, the corresponding chromocyclopentane stabilized by **10** (Cr-L10) shows a distorted tetrahedral geometry. Besides, one of the two phosphines is barely coordinating and **10** can better be regarded as a monodentate ligand (Cr-L10*, $\Delta G_{\text{Cr-L10*, 298 K}} - \Delta G_{\text{Cr-L10, 298 K}} = -4.9$ kcal/mol). The vacant site created by the leaving phosphine is then available for the third ethylene to coordinate. We speculate that loss of the bidentate character of ligand **10** might be the reason that the Cr/**10** system lost its selectivity towards 1-hexene or 1-octene (Scheme 2). Nevertheless, the possibility should not be preculded that active species differing from Cr-L10 is generated from Cr/**10** system, which also enables non-selctive ethylene oligomerization.

Conclusions

Of a series of diphenylphosphine-substituted N-hetrocyclic ligands, N-pyrrolyldiphenylphosphine proved to afford a selective ethylene oligomerization catalyst when *in situ* mixed with $Cr(acac)_3$ and aluminum-based co-catalysts in methylcyclohexane, producing 1-hexene and 1-octene with an overall selectivity up to 99 % together with a small amout of PE. In this system, the 1-hexene/1-octene ratio can be tuned from 0.3 to 20 by the choice and amount of solvents and co-catalysts, as well as by varying the reaction conditions such as temperature, pressure and ligand/Cr ratio. The most striking feature is the positive effect of the presence of small volume percentages of toluene on the 1-octene selectivity for the methylcyclohexane-based oligomerizations. When increasing the amount of toluene (> 10 volume-%) non-selective ethylene oligomerization becomes prominent and in pure toluene more or less a statistic distribution of oligomers is obtained. By careful adjustment of the reaction conditions, 1-hexene and 1-octene selectivites of up to 91 % and 74 %, respectively, with fairly good activities could be achieved. Coupling two units of ligand **7** proved to be unfavorable for improving the 1-hexene or the 1-octene selectivity, which is probably due to the monodentate rather than bidentate bonding mode of the ligand as revealed by DFT calculations.

Experimental Section

General Procedures: All manipulations for air and/or moisture sensitive materials were carried out under inert atmosphere in a glovebox or using Schlenk techniques. Dry solvents were obtained by passing them through a column purification system. Starting materials for ligand synthesis were purchased from Sigma-Aldrich and used as received. MAO (10 wt% toluene solution) was purchased from Aldrich and used as received. DMAO was prepared by pumping off all the volatile compounds of MAO at 40 °C for 6 hours. All NMR spectra were recorded on Varian Mercury 400 or 500 MHz spectrometers at 25 °C.

Ligand synthesis:

N-carbazolyldiphenylphosphine (**1**) was prepared following the method from the literature.[59] ^{31}P NMR (400 MHz, CDCl$_3$) δ: 31.68 (s). Purity 97 % on the basis of ^{31}P NMR.

Phenylbis(1-carbazolyl)phosphine (**2**) was prepared following the method from the literature.[59] ^{31}P NMR (400 MHz, $CDCl_3$) δ: 51.78 (s). Purity 94 % on the basis of ^{31}P NMR.

N-indolyldiphenylphosphine (**3**): *n*-BuLi (4.0 mL, 10 mmol, 2.5 M in hexane) was added dropwise to a stirred THF solution (20 mL) of indole (1.18 g, 10 mmol) at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. Petroleum ether (15 mL) was added to precipitate a white powder, which was isolated by filtration, washed with petroleum ether twice and then redissolved in THF (40 mL). Ph_2PCl (1.8 mL, 10 mmol) was added dropwise at 0 °C and the reaction mixture was stirred overnight. The solvent was evaporated under reduced pressure and the resulting oil was dissolved in toluene. The suspension was filtered and the solvent was removed *in vacuo*. The product was crystallized from petroleum ether as colorless crystals (2.4 g, 8.0 mmol, 80 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, 1H), 7.62 (d, 1H), 7.43-7.29 (m, 10H), 7.20 (d, 1H), 7.17 (d, 1H), 6.98 (t, 1H), 6.64 (d, 1H). ^{31}P NMR (400 MHz, $CDCl_3$) δ: 35.20 (s). ^{13}C NMR (500 MHz, $CDCl_3$) δ: 141.3, 136.3, 134.3, 132.1, 130.5, 130.2, 129.7, 128.8, 128.2, 122.2, 120.8, 112.3, 106.5. Purity 99 % on the basis of ^{31}P NMR.

Phenylbis(1-indolyl)phosphine (**4**): As for **3** using indole (2.35 g, 20 mmol), *n*-BuLi (8.0 mL, 20 mmol, 2.5 M in hexane) and $PhPCl_2$ (1.4 mL, 10 mmol). Recrystallization from petroleum ether gave colorless crystals (2.1 g, 6.2 mmol, 62 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (d, 2H), 7.60 (d, 2H), 7.48-7.38 (m, 4H), 7.30-7.25 (m, 2H), 7.21-7.15 (m, 5H), 7.66 (d, 2H). ^{31}P NMR (400 MHz, $CDCl_3$) δ: 48.62 (s). ^{13}C NMR (500 MHz, $CDCl_3$) δ: 141.1, 134.9, 131.0, 130.4, 130.2, 129.0, 128.9, 122.9, 121.5, 112.1, 108.0. Purity 99 % on the basis of ^{31}P NMR.

N-pyrazolyldiphenylphosphine (**5**): A Schlenk flask was charged with pyrazole (3.40 g, 50 mmol), triethylamine (7.4 mL, 52.5 mmol), and THF (85 mL). Subsequently, Ph_2PCl (9.0 mL, 50 mmol) was added dropwise at 0 °C and the solution was stirred overnight at room temperature. The colorless precipitate which formed was removed by filtration and was washed with THF. The solvent was removed *in vacuo* to give the product as an oil (7.6 g, 30 mmol, 60 %). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, 1H), 7.68 (t, 1H), 7.43-7.35 (m, 10H), 6.38 (t, 1H). ^{31}P NMR (400 MHz, $CDCl_3$) δ: 54.24 (s). ^{13}C NMR (500 MHz, $CDCl_3$) δ: 144.5, 136.9, 136.3, 132.6, 130.1, 128.6, 107.2. Purity 96 % on the basis of ^{31}P NMR.

Phenylbis(1-pyrazolyl)phosphine (**6**): A Schlenk flask was charged with pyrazole (4.36 g, 60 mmol), triethylamine (9.0 mL, 64.6 mmol), and THF (100 mL). This was followed by dropwise addition of Ph_2PCl (4.0 mL, 30 mmol) at 0 °C. The solution was stirred overnight at room temperature. The colorless precipitate which formed was removed by filtration and was washed with THF. The combined filtrates were dried *in vacuo*. The resulting oil was redissolved in petroleum ether and filtered. The solvent was removed *in vacuo* giving the resulting product as an oil (6.0 g, 25 mmol, 83 %). ^1H NMR (400 MHz, $CDCl_3$) δ: 8.10-7.76 (m, 4H), 7.71-7.32 (m, 5H), 6.41 (m, 2H). ^{31}P NMR (400 MHz, $CDCl_3$) δ: 73.03 (s). ^{13}C NMR (500 MHz, $CDCl_3$) δ: 145.1, 136.9, 135.1, 130.7, 128.8, 108.3. Purity 96 % on the basis of ^{31}P NMR.

N-pyrrolyldiphenylphosphine (**7**) was prepared following the method from the literature.[60] ^{31}P NMR (400 MHz, $CDCl_3$) δ: 47.73 (s). Purity 94 % on the basis of ^{31}P NMR.

Phenylbis(1-pyrrolyl)phosphine (**8**) was prepared following the method from the literature.[60] ^{31}P NMR (400 MHz, toluene-d_8) δ: 70.03 (s). Purity 99 % on the basis of ^{31}P NMR.

Diphenylbis(pyrrolyldiphenylphosphino)methane (**9**): A solution of benzophenone (27.0 g, 150 mmol) and methanesulfonic acid (0.5 mL) in 99 % ethanol was stirred and heated at 60-70 °C until complete dissolution. Neat pyrrole (10 mL, 140 mmol) was added over a period of 30 min and the mixture was stirred at 60-70 °C for 4 h, upon which the color of the solution changed from dark red to dark brown. The mixture was diluted with 99 % ethanol (100 mL) and allowed to crystallize at 50 °C. A red solid was obtained, which was filtered and washed with portions of warm ethanol (100 mL, 50 °C) until complete discoloration followed by drying *in vacuo* (5.8 g, 19.5 mmol, 13 %). The solid diphenyldipyrrolylmethane was then dissolved in THF (65 mL). *n*-BuLi (15.6 mL, 39 mmol, 2.5 M in hexane) was added over a period of 20 min at -78 °C. After stirring overnight at room temperature, chlorodiphenylphosphine (7.2 mL, 39 mmol) was then added dropwise at 0 °C. After stirring overnight at room temperature, the solvent was pumped off *in vacuo*. The resulting oil was redissolved in toluene and insoluble material was removed by filtration. The clear solution was dried *in vacuo* and the oily residue was dissolved in petroleum ether. Beige powder was collected after filtration and drying *in vacuo* (5.6 g, 8.4 mmol, 43 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31-6.99 (m, 30H), 6.71 (q, 1H), 6.49 (q, 1H), 6.17 (q, 1H), 6.13 (q, 1H), 6.04 (q, 1H), 5.83 (q, 1H). ^{31}P NMR (400 MHz, $CDCl_3$) δ: 36.73 (s). ^{13}C NMR (500 MHz, $CDCl_3$) δ: 145.8, 137.8, 132.4, 129.9, 129.0, 128.0, 127.4, 126.3, 116.8, 114.4, 109.6, 107.9. Purity 95 % on the basis of ^{31}P NMR.

Diethylbis(pyrrolyldiphenylphosphino)methane (**10**): 37 % aqueous HCl (0.5 mL) was added to a solution of 3-pentanone (15 mL, 0.14 mol) in boiling water (100 mL), which was followed by the dropwise addition of neat pyrrole (5.0 mL, 0.7 mol). After refluxing for 45 min the suspension was left to cool to 40–50 °C and then the upper layer was collected and allowed to cool to room temperature upon which crystals precipitated. The green crystals were separated by filtration and redissolved in an ethanol/water mixture. The solution was left overnight at room temperature and colorless crystals formed. The white crystals were filtered, washed with ethanol/water and dried overnight in a vacuum oven (40 °C) (4.1 g, 20 mmol, 14.5 %). The dried diethyldipyrrolylmethane (2.0 g, 10 mmol) and triethylamine (3.5 mL, 25 mmol) were dissolved in THF (30 mL). PPh_2Cl (3.5 mL, 20 mmol) was then added dropwise at 0 °C. After reflux overnight at 70 °C, the formed white solid was removed by filtration and the filtrate was dried *in vacuo* yielding brown oil. The resulting oil was redissolved in petroleum ether and stirred overnight. Beige powder was collected after filtration and drying *in vacuo* (2.3 g, 4.0 mmol, 40 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43-7.19 (m, 22H), 6.27 (q, 2H), 6.06 (m, 2H), 1.84 (q, 4H), 0.66 (t, 6H). ^{31}P NMR (400 MHz, $CDCl_3$) δ: -27.00 (s). ^{13}C NMR (500 MHz, $CDCl_3$) δ: 140.9, 137.7, 132.7, 128.5, 128.4, 123.1, 118.8, 107.9, 44.1, 30.0, 8.4. Purity 83 % on the basis of ^{31}P NMR.

Ethylene Oligomerization: All the ethylene oligomerization tests were performed in a 200 mL Büchi autoclave. The autoclave was heated in an oven at 150 °C overnight before each run. After evacuation and rinsing with argon three times, the solvent (volume of solvent = total volume (100 mL) - volume of catalyst solution - volume of co-catalyst solution) was charged into the preheated autoclave. Then the co-catalyst was injected and the solvent was saturated with ethylene by pressurizing to 30 bar. After 15 minutes of stirring, the autoclave was temporarily vented to allow the injection of the catalyst solution. The autoclave was repressurized to the desired pressure and the pressure was maintained throughout the run. The temperature of the autoclave was controlled by a thermostatted bath. After 30 minutes, the reaction was quenched by cooling to 0 °C, depressurizing and injection of a mixture of ethanol and diluted hydrochloric acid. The polymer was separated by filtration and dried overnight at 60 °C under reduced pressure before mass determination. The oligomers were analyzed by GC-FID for oligomer composition and by ^{1}H NMR spectroscopy for activity. Since the activity was measured for 0.5 h and there was a catalyst decay after 15 min indicated by the temperature drop, it should be noted that the real productivity per hour might be lower than the calculated data.

Computational details: All the DFT calculations were performed using the Gaussian 09 program package.[61] Geometry optimizations were carried out without any symmetry constraints, using the unrestricted PBE density functional and Ahlrichs triple-ζ basis set TZVP. The nature of stationary points for all the resulting geometries was verified by analytical frequency calculations (no imaginary frequencies). Single-point energies were obtained at the same level of theory. All energies reported referred to Gibbs free energy corrections to the total electronic energies at 298.15 K.

ASSOCIATED CONTENT

Supporting Information.

Cartesian coordinates of all optimized chromacyclopentane structures in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

We'd like to thank the Chinese Scholarship Council, the Natural Science Foundation of China (No. 21174037) and the Eindhoven University of Technology for financial support.

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