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Evaluation of Bis(phosphine) Ligands for Ethylene Oligomerization: Discovery of Alkyl Phosphines as Effective Ligands for Ethylene Tri- and Tetramerization

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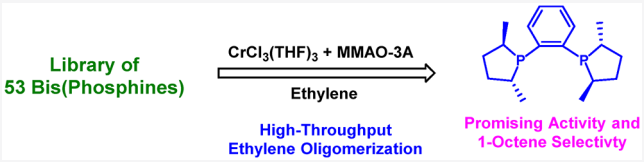
ABSTRACT: Fifty-three bis(phosphines) were evaluated as ligands for chromium-catalyzed ethylene tetramerization in a high-throughput reactor. Selected ligands previously reported in the literature gave high activities with expected selectivities when evaluated under our reactor conditions. While the majority of ligands evaluated gave low activity catalysts that produced mostly high-density polyethylene (HDPE), alkyl phosphines were unexpectedly identified as a promising ligand class. In particular, the MeDuPhos ligand led to an active catalyst that produced 81.8 wt % α-olefins (50.0 wt % 1-octene, 31.8 wt % 1-hexene) and 3.5 wt % HDPE, approaching the selectivity of the state-of-the-art *i*-Pr-PNP ligand.



INTRODUCTION

The selective oligomerization of ethylene to linear α-olefin (LAO) products is an active area of research due to the extensive use of these short-chain α-olefins as comonomers with ethylene in the production of linear low-density polyethylene (LLDPE).[1] Linear α-olefins used in LLDPE production are conventionally obtained from the nonselective oligomerization of ethylene, which yields Schulz−Flory or Poisson distributions.[2] However, market demand is increasingly rendering the supply of short-chain LAOs from traditional sources inadequate.[1a]

Selective oligomerization technologies have emerged to answer the market demand for short-chain LAOs. Ethylene trimerization for the production of 1-hexene has been known since 1967, and the process to produce 1-hexene based on selective ethylene trimerization has been commercialized.[3] However, it was not until 2004 that catalysts capable of the selective tetramerization of ethylene to 1-octene were reported by researchers from Sasol Technology.[4] This first report described a Cr-based system with a bis(diphenylphosphino)-amine (PNP), bis(diphenylphosphino)hydrazine (PNNP), or a 1,2-bis(diphenylphosphino)ethane (dppe) ligand. Sasol's best example, utilizing bis(diphenylphosphino)isopropylamine (*i*-Pr-PNP, **1**), yielded 68.3 wt % 1-octene at 653 psi of ethylene and 45 °C.[4] The other major products of the catalysis were 1-hexene (16.9 wt %); cyclic C6 products (methylcyclopentane and methylenecyclopentane; 5.0 wt %); C10−C18 α-olefins (tri- and tetramer products of ethylene with 1-hexene and 1-octene; 8.7 wt %); and high-density polyethylene (HDPE; 1.1 wt %) (Scheme 1). While all non-α-olefin products are undesirable, the high-density polyethylene byproduct is of particular concern, as it is not soluble at the relatively low temperatures (<100 °C) used in the ethylene tetramerization process and therefore can lead to significant reactor fouling.

Since Sasol's initial report of the PNP/Cr tetramerization system, the search for tetramerization ligands that lead to catalysts with improved 1-octene selectivity and fewer undesirable byproducts has been an active area of research in both industrial and academic settings. Several chemical and oil companies in addition to Sasol, such as SK Energy,[5] Chevron Phillips Chemical,[6] ExxonMobil,[7] and Shell,[8] have been active in this area. Sasol has published several reports[4,9,10] describing the tetramerization capabilities of *i*-Pr-PNP derivatives. Interestingly, small changes in ligand structure have significant impact on both the activity and selectivity of the resulting chromium catalysts. For instance, replacing the *i*-Pr-N bridge in ligand **1** (Figure 1) with a Me-N bridge lowered the octene selectivity by 15.5 wt % and increased the amount of HDPE produced by a factor of 5.[10a] Furthermore, simply changing the *i*-Pr-N bridge to a CH_2 bridge (ligand **7**, Figure 1, Table 1) resulted in a ligand that no longer led to a competent tetramerization catalyst, but rather resulted in a low-activity catalyst that produced a Schulz−Flory distribution of LAOs.[10b]

Outside the PNP ligand family, a variety of two- and three-carbon-bridged, diphenyl phosphine-based ligands have proven

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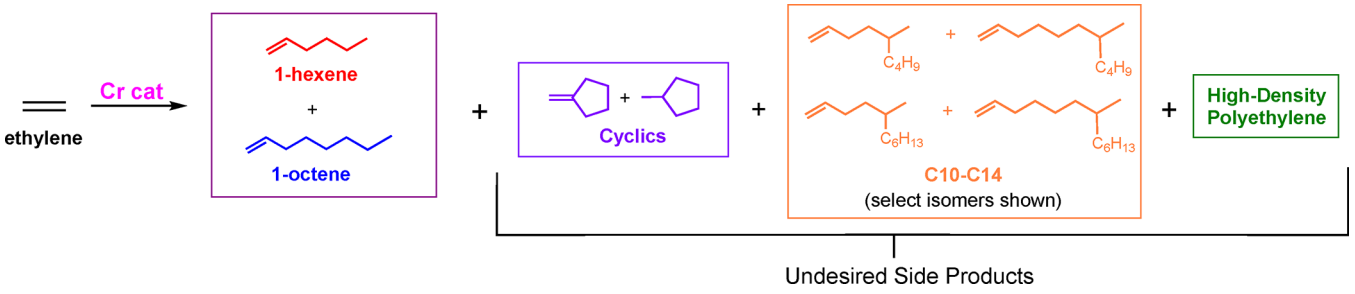
Scheme 1. Major Reaction Products of Chromium-Catalyzed Ethylene Tetramerization



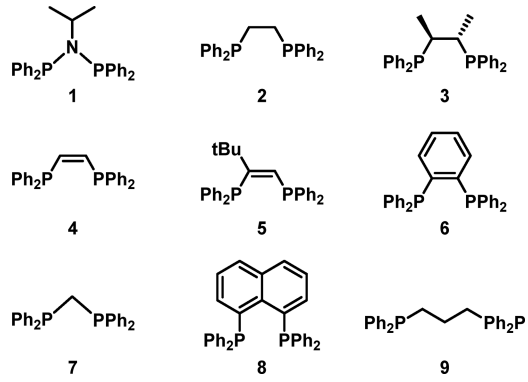


Figure 1. Structures of selected ligands previously studied for chromium-catalyzed ethylene tetramerization.

Table 1. Literature Values for Chromium-Catalyzed Ethylene Tetramerization with Selected Ligands

	activity[a]	selectivity[b]		
ligand #	(g product/g Cr h)	1-octene	1-hexene	HDPE
1[10a,c]	1 950 000	69.5	16.8	0.9
2[10b,d]	144 000	59.3	15.7	4.9
3[5b,e]	1 929 000	59.2	31.4	0.7
4[10b,d]	303 000	46.7	7.3	5.2
5[11,f]	1 926 000	40.4	39.8	0.1
6[10b,d]	2 240 000	56.8	13.0	0.9
7[10b,d]	21 000	Schulz–Flory Distribution of LAOs		
8[10b,d]	70 000	31.4	61.9	4.0
9[10b,d]	13 000	30.3	8.6	24.3

[a]Activities are highly conditions-dependent, making comparisons across different reports difficult. [b]Selectivity is dependent on both temperature and pressure. At higher pressures and lower temperatures, 1-octene selectivity is higher. Selectivities are given for three of the five major reactor products (1-octene, 1-hexene, and HDPE). The two other major reaction products are C10–C18 α-olefins and cyclic products (methylcyclopentane and methylenecyclopentane). [c]Conditions: 2.5 μmol $Cr(acac)_3$, 3 μmol ligand, MMAO-3A:Cr = 300:1, 60 °C, 653 psi ethylene, 100 mL methylcyclohexane. [d]Conditions: 5–30 μmol Cr, MMAO-3A:Cr = 500:1, 60 °C, 725 psi ethylene, 100 mL methylcyclohexane. [e]Conditions: 2.5 μmol catalyst, MMAO-12A:Cr = 300:1, 45 °C, 435 psi ethylene, 150 mL methylcyclohexane. [f]Conditions: 1.0 μmol precatalyst, MMAO-3A:Cr = 500:1, 40 °C, 580 psi ethylene, 30 mL methylcyclohexane.

capable of giving active tetramerization systems with chromium. Sasol has described the use of dppe (**2**), 1,3-bis(diphenylphosphino)propane (**9**, dppp), and 1,2-bis-(diphenylphosphino)ethene (**4**) as ligands for chromium-catalyzed ethylene tetramerization.[10b] SK Energy described the use of (*S*,*S*)-chiraphos (**3**, Figure 1) as advantageous over *i*-Pr-PNP due to greater catalyst longevity.[5] Despite the reported high activities and low amounts of HDPE formed, this catalyst and similar derivatives, such as the catalyst using the $Ph_2PC(t\text{-}Bu)=CHPPh_2$ (**5**, Figure 1) ligand described by the Shi group (Table 1), did not reach the 1-octene selectivities of the chromium catalyst with *i*-Pr-PNP (**1**).[11]

Whether a catalyst favors the formation of 1-octene or 1-hexene is known to be influenced by the steric bulk of the ligand, with less sterically encumbering catalysts leading to higher 1-octene selectivities.[10f] Along these lines, among ligands with three-carbon bridges between the phosphines, the selectivity of the resulting catalysts appears to be somewhat dependent on the rigidity of the bridging group. When a rigid linker, such as in 1,8-bis(diphenylphosphino)naphthalene (**8**, Figure 1, Table 1), is employed, a switch to an ethylene trimerization catalyst is observed, presumably because ligand steric constraints prevent the formation of the larger metallacycle intermediate that leads to 1-octene.[10b] In contrast, the more flexible 1,3-bis(diphenylphosphino)propane ligand (**9**, Figure 1, Table 1) results in the production of more 1-octene than 1-hexene.[10b]

While most of the ligands described for use in tetramerization catalysis employ two diphenylphosphine groups to coordinate to the Cr center, there are a few examples of ligands with other coordinating groups that lead to active tetramerization catalysts. These ligands typically lead to lower activity catalysts that produce higher levels of HDPE. The most successful of these ligands is a phosphine-amidine ligand from Chevron that led to a catalyst that exhibited not only moderate activity and relatively low HDPE formation, but also relatively low octene selectivity.[6,12] Other ligands with N-coordinating groups gave catalysts with low activity and led to high HDPE levels.[7,13]

Given the greater success of bis(phosphine)-based ligands over other ligand families for ethylene tetramerization, we chose to focus our search for new tetramerization catalysts within this ligand class. This paper describes the evaluation of 53 bis(phosphine) ligands with varying steric and electronic attributes, as it has been demonstrated that small changes in ligand structure can lead to significant changes in the activity and selectivity of the resulting catalysts.[4] Unexpectedly, we discovered that some alkyl phosphines can lead to very active Cr-based catalysts that exhibit high selectivities toward 1-octene and 1-hexene.

RESULTS AND DISCUSSION

Bidentate diphenylphosphine-based ligands were selected as the main focus of this study due to the already established success of such compounds in ethylene tetramerization

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catalysis and the commercial availability of a diverse range of ligands in this class. A series of bidentate alkyl phosphines was also included in this study to augment the diversity of ligand electronic parameters. The 53 ligands thus selected were assessed in a high-throughput reactor (HTR) that has 24, 14 mL reactors and is housed in a nitrogen-filled drybox. Uniform conditions of 0.05 μmol of $CrCl_3(THF)_3$ and 0.06 μmol of ligand (1.2 equiv relative to Cr) were used, with 50 μmol of MMAO-3A (Al:Cr ratio of 1000:1) as the activator.

Precatalyst solutions were prepared by mixing a 1.0 mM solution of bis(phosphine) ligand and a 1.0 mM solution of $CrCl_3(THF)_3$, both in chlorobenzene for 30 min. Active catalysts were then generated in situ by adding precatalyst solutions to a MMAO-3A methylcyclohexane solution (50 mM) at ambient temperature and pressure. Oligomerization reactions were carried out at an ethylene pressure of 500 psi and a temperature of 60 °C for 30 min. Methylcyclohexane (4 mL total volume) was the primary reaction solvent in this study. In order to achieve high oligomerization activities, it is imperative to employ rigorously purified solvents and reagents as we found that, despite the use of a relatively high level of MMAO-3A, small amounts of impurities in solvents and gas feeds can dramatically lower activity or even completely shut down this catalytic process.

The catalyst loading used here allowed for the evaluation of both high activity catalysts and lower activity catalysts, as enough product was made even by the lower activity catalysts for meaningful analysis. Liquid products from these reactions were analyzed by gas chromatography while the mass of the HDPE byproduct[15] was measured gravimetrically. The state-of-the-art *i*-Pr-PNP (**1**) ligand was included in every screened ligand library as a reference against which all other ligands were compared (Tables 2−3, Figures 1−4). While the majority of ligands in this investigation had not been previously studied in the context of ethylene oligomerization, some ligands reported in the literature to give active oligomerization catalysts were included in this study. Importantly, not only did these ligands lead to active catalysts under our conditions, they also gave similar selectivities to those provided in literature reports, thus validating our experimental setup. For example, the state-of-the-art *i*-Pr-PNP (**1**) ligand led to a catalyst with a high activity of 492 000 g product/g Cr h with a selectivity of 62.0 wt % 1-octene, 24.9 wt % 1-hexene, and 2.2 wt % HDPE (compare with literature values in Table 1: 69.5 wt % 1-octene, 16.8 wt % 1-hexene, and 0.9 wt % HDPE). The known oligomerization catalysts with two-carbon bridges in the bis(phosphine) backbone (Table 2; ligands **2**−**4** and **6**) also performed similarly to those described in the literature reports. Selectivity trends in newly evaluated ligands with two-carbon bridges followed the steric trends reported in the literature,[10f] in which bulkier ligands led to greater 1-hexene formation and less 1-octene. While dppe (**2**) leads to a catalyst that primarily tetramerizes ethylene, giving 53.7 wt % 1-octene under our conditions, ligand **12**, in which an *o*-methyl substituent was added to two of the four dppe phenyl groups, gives a catalyst that primarily trimerizes ethylene, giving 52.7 wt % 1-hexene with an activity about half that of dppe (**2**) (Table 2). Ligand **11**, which has two *o*-methoxy substituents appended to the dppe framework, led to an excellent ethylene trimerization catalyst. With an activity of 529 000 g product/g Cr h and with selectivities of 97.2 wt % 1-hexene and 0.8 wt % HDPE, under our conditions it gives superior 1-hexene selectivity and comparable HDPE formation to the *o*-OMe PNP ligand (ligand **10**) developed by British Petroleum.[16]

Table 2. High-Throughout Ethylene Oligomerization Using Selected Bis(phosphine) Ligands

			selectivity[a,b,c] (wt%)		
ligand #	product yield[a,b] (mg)	activity[a,b] (g product/g Cr h)	1-octene	1-hexene	HDPE
1	639.4	492 000	62.0	24.9	2.2
2	206.7	159 000	53.7	23.5	8.6
3	726.7	559 000	52.4	35.2	3.2
4	274.5	211 000	45.4	13.0	11.0
6	590.1	454 000	55.6	22.3	5.5
10	1270.8	978 000	4.7	90.4	0.6
11	688.6	529 000	0.4	97.2	0.8
12	78.4	60 000	8.0	52.7	35.3
13	8.6	7000	2.0	2.5	92.4
14	144.4	111 000	0.3	16.3	81.1
15	144.3	111 000	7.1	12.3	46.2
16	204.7	157 000	1.2	0.2	97.8
17	60.3	46 000	9.9	67.6	16.5
18	8.8	6000	5.1	11.8	69.0
19	8.5	6000	1.3	1.3	94.3
20	150.3	114 000	41.5	12.7	7.1
21	28.2	22 000	3.2	67.2	24.6
22	79.2	61 000	35.7	12.9	10.1
23	453.2	349 000	33.9	48.1	1.5
24	10.7	8000	0.0	26.8	67.9
25	40.0	31 000	0.0	78.3	19.0
26	116.6	90 000	1.2	79.6	14.8
27	240.2	185 000	50.0	31.8	3.5

[a]Averaged over two replicates. [b]Product yield and activity and selectivity calculations include all major reaction products: 1-octene, 1-hexene, HDPE, cyclic C6 products (methylcyclopentane and methylenecyclopentane), and C10−C18 α-olefin compounds. Sample calculations are provided in the Supporting Information. [c]Selectivities for the main products of interest (1-octene, 1-hexene, and HDPE) are given here. The amounts of the cyclic products (methylcyclopentane and methylenecyclopentane) and higher α-olefin products (C10−C18) were quantified to obtain complete mass balance. Complete information on reaction products can be found in the Supporting Information.

Incorporating additional coordinating groups in ligands that lead to successful oligomerization catalysts tends to greatly diminish their activity and lead to the formation of high levels of HDPE. For instance, replacing the *i*-Pr-N bridge in *i*-Pr-PNP (**1**) with a 2-pyridyl-N bridge (**29**, Table 3, Figure 4) leads to a 16-fold decrease in activity and a switch in selectivity to a polymerization catalyst that yields 87.7 wt % HDPE. Given that the PNP derivative with a *p*-tolyl-N bridge is known to give a successful ethylene tetramerization catalyst,[10d] it must be the inclusion of a pyridyl group and not the alkyl-to-aryl switch that causes the activity and selectivity change. Similarly, changing the phenyl groups in dppe (**2**) to 2-pyridyl groups (ligand **13**) leads to a catastrophic 24-fold decrease in catalytic activity with a selectivity of 92.4 wt % HDPE. The most surprising ligand class to emerge from this study was that of the alkyl phosphines. Given that most successful tetramerization catalysts have relatively electron-withdrawing (i.e., phenyl) substituents on the phosphorus atoms, this ligand class was not expected to yield very productive catalysts based on previous studies.[10b] However, this class of ligands has unexpectedly

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Table 3. High-Throughout Ethylene Oligomerization Using Selected Bis(phosphine) Ligands

ligand #	product yield[a,b] (mg)	activity[a,b] (g product/g Cr h)	selectivity[a,b,c] (wt %) 1-octene	1-hexene	HDPE
28	60.5	46 000	37.3	6.7	23.7
29	39.4	30 000	2.8	5.8	87.7
30	21.2	16 000	21.6	11.1	51.1
31	282.2	217 000	52.2	26.6	7.8
32	668.4	514 000	53.4	35.0	2.3
33	78.1	60 000	0.5	18.4	77.2
34	43.0	33 000	1.5	1.7	85.5
35	46.0	35 000	0.5	20.3	71.4
36	25.3	19 000	0.7	11.6	82.2
37	8.0	6000	2.3	5.4	85.1
38	11.8	9000	2.3	2.5	88.9
39	16.3	13 000	2.2	2.8	77.6
40	18.0	14 000	0.5	1.1	96.2
41	80.8	62 000	27.1	6.5	49.3
42	93.4	72 000	0.3	0.7	96.4
43	13.3	10 000	0.4	54.4	41.3
44	16.9	13 000	3.1	8.2	70.1
45	5.9	5000	0.7	2.6	92.6
46	7.6	6000	0.0	6.3	88.5
47	20.3	16 000	6.2	8.8	56.0
48	54.2	42 000	9.0	9.4	40.3
49	9.4	7000	0.7	1.9	94.8
50	9.9	8000	1.3	1.7	91.7
51	17.2	13 000	5.6	14.5	51.7
52	8.2	6000	1.4	9.2	68.5
53	10.4	8000	3.1	10.6	70.3
54	5.7	4000	0.9	1.0	95.3
55	8.3	6000	0.5	1.6	89.9
56	6.8	5000	0.0	2.7	91.7
57	28.0	22 000	0.0	67.3	29.8

[a]Averaged over two replicates. [b]Product yield and activity and selectivity calculations include all major reaction products: 1-octene, 1-hexene, HDPE, cyclic C6 products (methylcyclopentane and methylenecyclopentane), and C10−C18 α-olefin compounds. Sample calculations are provided in the Supporting Information. [c]Selectivities for the main products of interest (1-octene, 1-hexene, and HDPE) are given here. The amounts of the cyclic products (methylcyclopentane and methylenecyclopentane) and higher α-olefin products (C10−C18) were quantified to obtain complete mass balance. Complete information on reaction products can be found in the Supporting Information.

provided the most promising leads for further study. While ligands containing dimethylphosphino (**19**,[10b] **22**) and diisopropylphosphino (**21**, **24**)[10b] fragments led to low activity catalysts as reported previously, we found that analogous ligands containing diethylphosphino groups (**20** and **23**) are considerably more active and exhibit 1-octene selectivities of 41.5 and 33.9 wt %, respectively, which is respectable especially in light of the lower levels of HDPE produced (7.1 and 1.5 wt %, respectively). Thus, the diethylphosphino group appears to be an advantaged motif among these two-carbon-bridged ligands for Cr-catalyzed ethylene tetramerization. Given that the electronic differences between methyl, ethyl, and isopropyl substituents are relatively small, we can hypothesize that there are steric reasons for these different catalytic behaviors. The selectivity trend across these phenylene-bridged bidentate alkyl phosphine ligands is as expected:[10f] the dimethylphosphine-based ligand **22** gives the highest 1-octene selectivity, while the bulkier methyl/*t*-butyl-phosphine ligand **25** gives the highest 1-hexene selectivity.

The most promising alkyl phosphine evaluated in this study is MeDuPhos (**27**). Comprising two five-membered phosphacycles known as phospholanes, the MeDuPhos ligand (**27**) is structurally distinct from ligands used in conventional diphenylphosphine-based ethylene oligomerization catalysts. While under the conditions used here MeDuPhos (**27**) led to a catalyst with about half the activity of the catalyst formed from the benchmark *i*-Pr-PNP (**1**), the selectivity for the desired products was impressive. At 50.0 wt % 1-octene, 31.8 wt % 1-hexene, and 3.5 wt % HDPE, the combined selectivity of useful products 1-octene and 1-hexene (81.8 wt %) of this catalyst approaches that of *i*-Pr-PNP (**1**) (86.9 wt % 1-octene + 1-hexene). Furthermore, the 3.5 wt % HDPE observed for this catalyst is one of the lowest levels of HDPE produced by a catalyst outside the PNP family.

CONCLUSION

The high-throughput evaluation of 53 bidentate phosphine ligands led to the identification of a novel class of phosphine ligands that give active ethylene tetramerization catalysts with chromium. While selectivity trends reported in the literature in which increased steric bulk shifted selectivity from 1-octene to 1-hexene were observed for some of the newly evaluated ligands, most of the diphenylphosphine-based ligands studied here led to low activity catalysts that produce high levels of HDPE. In contrast, select bidentate alkyl phosphines were identified as active oligomerization catalysts with chromium. While diethylphosphine-based ligands (**20** and **23**) led to high catalytic activities unlike their dimethyl- and diisopropylphosphine analogues (**19**, **21**, **22**, and **24**), they favored 1-hexene over 1-octene production. Out of all alkyl phosphine ligands screened, the MeDuPhos ligand (**27**) led to a catalyst that unexpectedly exhibited the best combination of activity and 1-octene selectivity. This ligand produced a catalyst with good activity—about half the activity of the benchmark *i*-Pr-PNP ligand—and excellent selectivity: 50.0 wt % 1-octene, 31.8 wt % 1-hexene, as well as one of the lowest levels of high-density polyethylene (3.5 wt %) outside of the PNP ligand family. Structurally, MeDuPhos (**27**) is unique from ligands used in known ethylene oligomerization catalysts, most of which are based on a diphenylphosphine motif. The discovery of alkyl phosphines, and specifically the MeDuPhos ligand (**27**), enabled by high-throughput research, as effective ligands for ethylene tetramerization will open new avenues into ethylene tetramerization research. The preparation and ethylene oligomerization evaluation of chromium complexes with bis(phospholanes) and related ligands will be the focus of our next contribution.[17]

EXPERIMENTAL SECTION

General Methods. All solvents and reagents were used as received from commercial sources unless otherwise noted. Bis(phosphines) **2**−**6**, **11**−**15**, **17**−**21**, **25**−**29**, **31**, **33**−**36**, **38**−**52**, **54**, **55**, **57**, and bis(dichlorophosphino)benzene were purchased from Strem. Bis(phosphines) **16**, **30**, **32**, **53**, and **56** were purchased from Sigma-Aldrich. Commercial ligands were used without purification. For an indication of the level of purity of commercial ligands, all purchased compounds were evaluated by ^{1}H and ^{31}P NMR spectroscopy (see SI for NMR spectra). Bis(phosphines) **1**,[4] **10**,[18]

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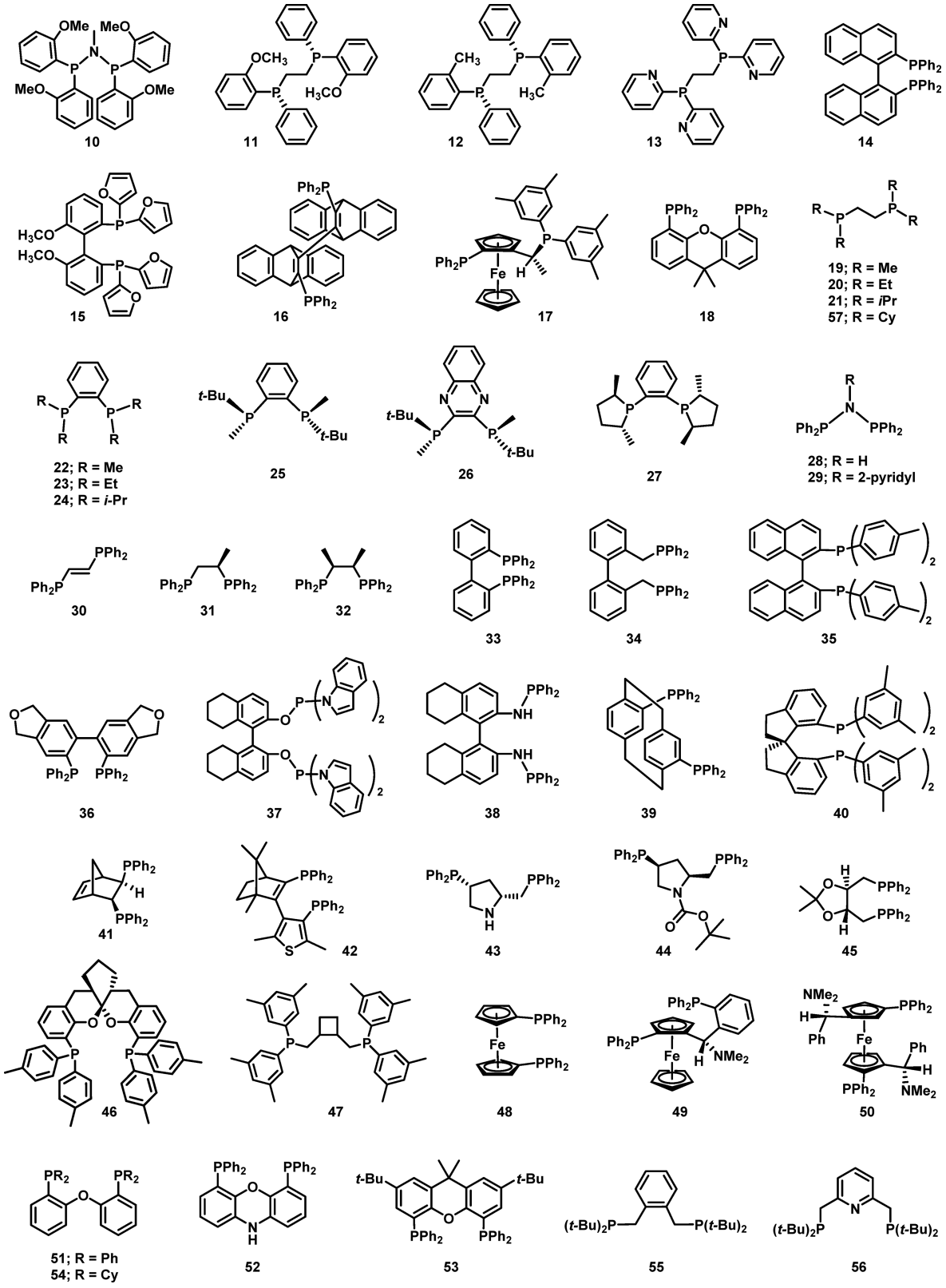

Figure 2. Bis(phosphine) ligands screened in this study.[14]

24,[10b] and **37**[19] were prepared using modified literature procedures. Ligands **22** and **23** were made in an analogous fashion to ligand **24**.[10b] All syntheses and manipulations were carried out in a nitrogen-filled glovebox unless otherwise noted. Tetrahydrofuran and hexanes were dried and degassed via a solvent system that employed A2 alumina and Q5 reactant (finely divided copper on alumina). Deuterated solvents were purchased from Cambridge Isotopes. C_6D_6 was dried over Na/K and $CDCl_3$ was dried over activated 4 Å molecular sieves before use. NMR spectra were recorded on Varian MR-400 or VNMRS-500 MHz NMR spectrometers. Chemical shifts are referenced to residual protons in the deuterated solvent for ^{1}H NMR spectra and ^{31}P NMR spectra are referenced according to the

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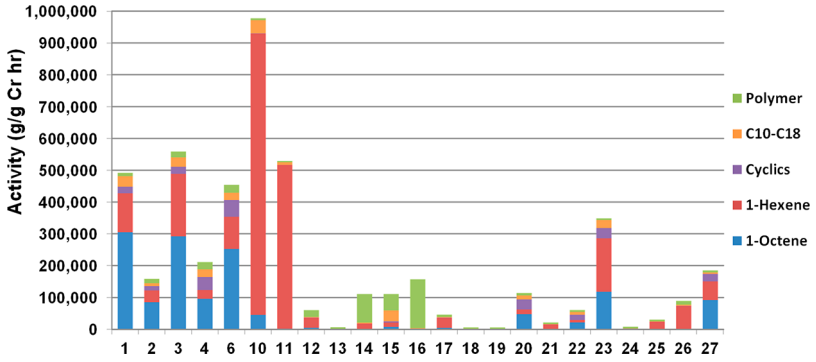


Figure 3. Ethylene oligomerization performance of bis(phosphine) ligands **1**−**4**, **6**, and **10**−**27**.

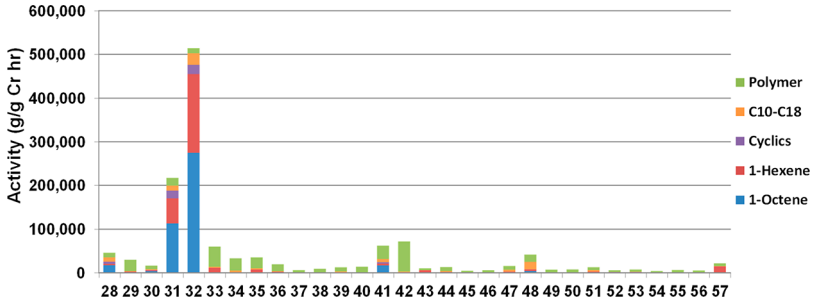


Figure 4. Ethylene oligomerization performance of bis(phosphine) ligands **28**−**57**.

IUPAC-recommended unified scale method.[20] High resolution mass spectrometry (HRMS) analyses were recorded on an Agilent Technologies 6230 TOF LC-MS coupled with a 1290 Infinity UPLC.

High-Throughput Experiments. All catalytic evaluations were performed using a high-throughput reactor housed in a nitrogen-filled glovebox in which reactions are performed in 24 individual reactor cells in a stainless-steel block fitted with glass inserts. All 24 reactors share a common headspace. Efficient mixing is achieved through the use of magnetic stir bars. The ethylene feed and the methylcyclohexane solvent were passed through purification columns containing A2 alumina (activated under nitrogen for 8 h at 300 °C) and Q5 reactant (Q5 reactant activated under 5% H_2 in argon for 1 h and then under nitrogen for 7 h at 200 °C). Chlorobenzene and nonane were purified by passing them through activated alumina. The methylcyclohexane, chlorobenzene, and nonane were stored over activated 3 Å molecular sieves (3 Å molecular sieves are activated under nitrogen for 4 h at 250 °C).

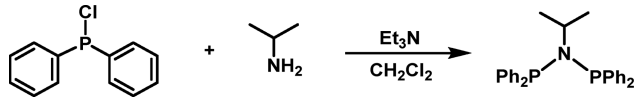
Precatalyst solutions were prepared in 8 mL vials by mixing the ligand and $CrCl_3(THF)_3$ in situ in chlorobenzene as follows: 120 μL of a 1.0 mM solution of $CrCl_3(THF)_3$ in chlorobenzene was combined with 144 μL of a 1.0 mM solution of the ligand in chlorobenzene in a 1:1.2 ratio in 8 mL vials. The samples were mixed for 30 min on a shaker prior to addition to the glass inserts.

Each glass insert was equipped with a magnetic stir bar, weighed, and charged with a predetermined amount of methylcyclohexane solvent via a liquid handler such that the final volume would be 4 mL. The liquid handler then delivered a solution of 10 wt % nonane (the GC internal standard in methylcyclohexane) for a total of 50 mg of nonane in each glass insert. 250 μL of an MMAO-3A solution (200 mM in methylcyclohexane, 50 μmol final loading), followed by 110 μL of precatalyst solution (0.05 μmol Cr final loading), were then added to the glass inserts via an Eppendorf pipet. One tube, used as a control, was charged as described above, except that precatalyst solution was not added. The glass tubes were inserted into the reactor that was subsequently sealed. The cells were pressurized with 100 psi of ethylene and heated to 60 °C, as monitored by five thermocouples in the stainless-steel block. Once the reaction temperature was reached, the cells were pressurized up to 500 psi with ethylene.

Each ligand was evaluated in duplicate in the high-throughput reactor. Furthermore, *i*-Pr-PNP (**1**) was included in each library as a positive control. Consistent activity and selectivity of this standard from run to run allowed for the catalysis results to be compared across high-throughput runs.

After 30 min, the reactions were terminated by stopping the ethylene feed and cooling to room temperature. The reactor was slowly vented at room temperature in order to limit loss of low-boiling analytes such as 1-hexene. A liquid sample was removed from each reaction for GC analysis, and the remainder of the liquid present was removed in vacuo on a Savant SC250EX SpeedVac Concentrator (Thermo Fisher). The glass tubes were then weighed to determine the amount of solids present. The weight of the residual solids from the control tube containing no catalyst solution was subtracted from the weight of the total residual solids in each reaction vial to yield the amount of polymer produced in each reaction.

*Synthesis of N-(Diphenylphosphino)-N-(1-methylethyl)-P,P-diphenyl-phosphinous amide (**1**).*



A glass jar containing 24.0 mL of chlorodiphenylphosphine (129.7 mmol, 2.2 equiv) and 67.5 mL of triethylamine (480.8 mmol, 8.2 equiv) dissolved in 50 mL of dichloromethane was cooled to −35 °C in a glovebox freezer. To this chilled solution was added 5.0 mL of isopropylamine (58.4 mmol, 1 equiv) slowly over the course of 15 min, causing the formation of a white precipitate. The resulting slurry was stirred for 24 h before it was filtered through a disposable filter and concentrated under reduced pressure giving an off-white solid. This off-white solid was recrystallized by dissolving it in 600 mL of hot ethanol, filtering, and allowing the solution to cool to room temperature. This yielded a first crop of white crystals, which were collected by vacuum filtration and washed on the filter with 20 mL of ethanol. The filtrate was placed in the freezer overnight, causing the precipitation of a second

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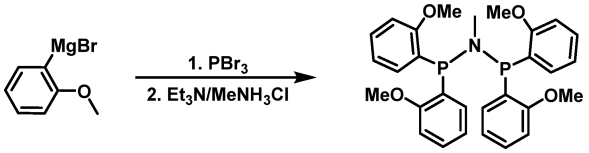
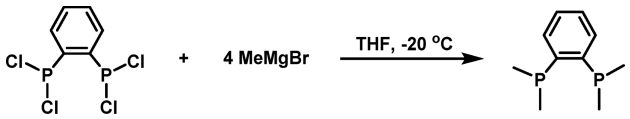
crop of white crystals, which were collected by vacuum filtration and washed on the filter with 20 mL of ethanol. The two batches of crystalline material were combined and dried further in vacuo, giving 19.44 g of a white crystalline solid (yield = 77.9%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.30 (m, 20H), 3.96−3.61 (m, 1H), 1.19 (d, J = 6.5 Hz, 6H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 48.80.

*Synthesis of N-[Bis(2-methoxyphenyl)phosphino]-P,P-bis(2-methoxyphenyl)-N-methyl-phosphinous amide (**10**).*



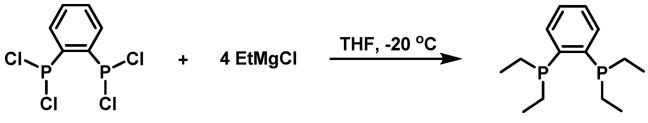
Fifteen mL of 2-methoxyphenylmagnesium bromide (15 mmol, 4 equiv, 1.0 M in THF) was added slowly to a cold (−78 °C) solution of 0.7 mL of PBr_3 (7.50 mmol, 2 equiv) dissolved in 85 mL of THF. The reaction mixture was stirred for 1.5 h before being warmed to room temperature and stirred for 18 h. 5.8 mL of triethylamine (41.3 mmol, 11 equiv) was then added via syringe followed by addition of 0.253 g of methylamine hydrochloride (3.75 mmol, 1 equiv) as a solid. The resulting white slurry was stirred for 24 h before it was concentrated under reduced pressure. Methanol (20 mL) was then added to the residue, which was stirred for 30 min. The resulting sold was collected via filtration, using nitrogen to push the solution through the filter to keep the atmosphere oxygen-free, and was dried in vacuo, giving 1.09 g of a white solid (yield = 56.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, J = 7.5 Hz, 4H), 7.14−7.05 (m, 4H), 6.87 (ddd, J = 8.8, 5.1, 2.1 Hz, 8H), 3.60 (s, 12H), 2.45 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 51.57.

*Synthesis of 1,1′-(1,2-Phenylene)bis[1,1-dimethylphosphine] (**22**).*



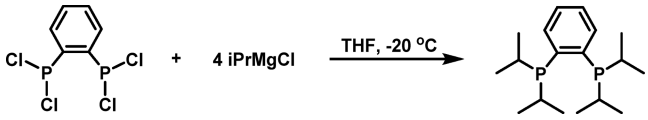
To a stirring solution of 1.2 g of 1,2-bis(dichlorophosphino)-benzene (4.29 mmol, 1 equiv) in 30 mL of THF at −20 °C was added 5.79 mL of a THF solution of methylmagnesium bromide (17.4 mmol, 4.05 equiv, 3 M) in a dropwise fashion. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The reaction mixture was then filtered and the solvent was removed in vacuo. The crude product was recrystallized from hot hexanes, giving 0.58 g of a pale yellow solid (yield = 53.2%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53−7.38 (m, 2H), 7.37−7.27 (m, 2H), 1.32 (s, 12H). ^{31}P NMR (162 MHz, $CDCl_3$) δ −54.7. HRMS (ESI-Q-TOF) m/z $[M + H]^+$ Calcd for $C_{10}H_{17}P_2$ 199.0698. Found: 199.0806.

*Synthesis of 1,1′-(1,2-Phenylene)bis[1,1-diethylphosphine] (**23**).*



To a stirring solution of 1.2 g of 1,2-bis(dichlorophosphino)-benzene (4.29 mmol, 1 equiv) in 30 mL of THF at −20 °C was added 8.7 mL of a THF solution of ethylmagnesium chloride (17.4 mmol, 4.05 equiv, 2 M) in a dropwise fashion. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The reaction mixture was then filtered and the solvent was removed in vacuo. The crude product was recrystallized from hot hexanes, giving 0.6 g of a pale yellow solid (yield = 55%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44−7.33 (m, 2H), 7.33−7.24 (m, 2H), 1.85−1.55 (m, 8H), 1.06−0.87 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.79−144.56 (m), 129.70 (t, J = 2.8 Hz), 128.15, 19.72 (t, J = 3.4 Hz), 9.67 (t, J = 6.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ −28.74. HRMS (ESI-Q-TOF) m/z $[M + H]^+$ Calcd for $C_{14}H_{35}P_2$ 255.1432. Found: 255.1425.

*Synthesis of 1,1′-(1,2-Phenylene)bis[1,1-bis(1-methylethyl)-phosphine] (**24**).*



To a stirring solution of 1.5 g of 1,2-bis(dichlorophosphino)-benzene (5.36 mmol, 1 equiv) in 30 mL of THF at −20 °C was added 11.0 mL of a THF solution of isopropylmagnesium chloride (21.98 mmol, 4.1 equiv, 2 M) in a dropwise fashion. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The reaction mixture was then filtered, and the solvent was removed in vacuo. The crude product was recrystallized from hot hexanes, giving 1.2 g of an off-white solid (yield = 72.5%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.45 (m, illl2H), 7.33−7.26 (m, 2H), 2.10 (hept, J = 7.0 Hz, 4H), 1.12 (q, J = 7.1 Hz, 12H), 0.88 (dd, J = 11.4, 6.9 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.83−143.95 (m), 132.46 (t, J = 2.1 Hz), 127.68, 24.91 (t, J = 5.5 Hz), 20.24 (br.), 19.45 (br.). ^{31}P NMR (162 MHz, $CDCl_3$) δ −4.77. The ^{31}P NMR chemical shift observed here is different than that reported previously for this bis(phosphine), whereas the ^{1}H and ^{13}C spectra are consistent with the reported data.[10b] HRMS (ESI-Q-TOF) m/z $[M + H]^+$ Calcd for $C_{18}H_{33}P_2$ 311.2058. Found: 311.2045.

General Quantitative Gas Chromatography (GC) Information. Quantitative GC analysis was performed using an Agilent 7890 Series instrument equipped with an Agilent DB-5MS column (30 m × 32 μm). The inlet was held at 300 °C, and the oven temperature was held at 70 °C for 8 min, followed by a 50 °C/min ramp to 300 °C, where the temperature was held for 3.4 min for a total run time of 16 min.

Samples for GC analysis were prepared by quenching 75 μL of the reaction mixture with 25 μL of methanol. The response factors were determined for 1-octene, 1-hexene, methylcyclopentane, and methylenecyclopentane via calibration using a standard solution with known concentrations. The response factors used for the C10 to C18 fractions were determined using the terminal olefin of the same carbon length (e.g., 1-decene for the C10 fraction). The concentrations of the reaction products were reported by the GC on a g/g nonane basis because nonane was included as an internal standard in the reaction tubes (50 mg nonane per 4 mL of reaction mixture). The amounts of the various reaction products produced were calculated relative to the amount of nonane added to the reaction mixture. For details, see the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00721.

Analytical details for ethylene oligomerization experiments, NMR spectra for all ligands studied, raw data for

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ethylene oligomerization studies, sample activity and selectivity calculations (PDF)

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Notes

The authors declare no competing financial interest.

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(14) Complete set of screening results is included in the Supporting Information.

(15) Some portion of the polyethylene produced may be waxy, lower molecular weight material. See: (a) Jiang, T.; Zhang, L.; Gao, J.; Cao, C. Hydrogen: Efficient Promoter for PNP/Cr(III)/MAO Catalyzed Ethylene Tetramerization Toward 1-Octene. *Appl. Petrochem. Res.* **2016**, *6*, 413−417. (b) Zoricak, P.; Brown, S. J.; Chisholm, P. S. Continuous Ethylene Tetramerization Process. WO2014/094114A1, December 12, 2012 (Nova Chemicals International S.A.).

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