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Efficient chromium-based catalysts for ethylene tri-/tetramerization switched by silicon-bridged/N, P-based ancillary ligands: A structural, catalytic and DFT study

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High performance catalysts switched by a series of silicon-bridged/N, P-based ancillary ligands have been explored. The precatalyst supported by **L1** possessed a large steric bulk and exhibited a high activity of 16.8×10^{6} g/(mol Cr·h) as well as a 99% total selectivity toward 1-hexene and 1-octene. The selectivity of 1-hexene was adjustable from 59% to 88%. The catalyst bearing **L2** ligand, facilitated by a smaller steric bulk, displayed an identical activity of 13.0×10^{6} g/(mol Cr·h) and a superior selectivity of 75% towards 1-octene under the appropriate conditions. The DFT calculations elucidated the reason for these excellent and tunable activities and selectivities.

Introduction

The PNP catalytic system for ethylene tetramerization was discovered by Sasol in 2004[1]. Because of its good commercial value and atom economy, the PNP system and, in particular, its ligands are being developed for selective ethylene oligomerization. Ligand selection is one of the most crucial and adjustable factors for selective ethylene tri- and tetramer switching[2-5]. Electronic and steric factors on N-substituted groups have been extensively scrutinized and explored in diverse catalytic systems for selective ethylene oligomerization[1, 6-15]. Moreover, the composition and length of PNP ligand have also been modified in search of an ideal catalytic system that is capable of producing 1-octene with high activity and selectivity[16-24]. Unfortunately, these traits, which was attempted to reach the performance obtained by well-developed ethylene trimerization catalytic systems((*e.g.,* the SNS catalytic system with an activity of 8.3×10^{6} g/(mol Cr·h) and selectivity of 98% towards 1-hexene)[25], are difficult to realize. However, new N, P-based ligands showed promise. Kim[22] and Gambarotta[21] reported chromium (III) complexes of chiral DPPDME and PN(C)nNP ligands that were capable of producing 77% and 88% selective 1-octene, respectively, with similar activities to the PNP catalytic system[1, 6]. It appears that ligands with diphosphorus favor ethylene tetramerization over

trimerization. Recently, we also reported a silicon-bridged diphosphine (SBDP) ligand system that could produce 78% selective 1-octene with 4.2×10^{6} g/(mol Cr·h) activity[26]. Compared to the phosphine-coordinated system, ligands with nitrogen linkers showed preferable activities[27-31]. Based on our previous studies, we hypothesized that introducing nitrogen into the backbone of a SBDP ligand may promote greater activity while maintaining selectivity towards 1-octene.

Herein, we describe a series of silicon-bridged/N, P-based (SBNP) ancillary ligands and their application in ethylene tri-/tetramerization catalysts. Density functional theory (DFT) calculations were also used to illustrate the excellent activity and selectivity of these systems.

Results and discussion

The target SBNP ligands **L1-L4** were first prepared by a convenient salt metathesis (**Figure 1**). Deprotonation by n-butyllithium and subsequent dropwise addition of chlorodiphenylphosphine converts primary amines to N, P-based units. Diphenylphosphanide was obtained from the diphenylphosphine and butyllithium treatment and was added to dichorodimethylsilane or dichloro(methyl)(phenyl)silane to produce Si, P-based units. The designed ligands were obtained by reacting the N, P-based units with n-butyllithium, followed by dropwise addition of Si, P-based units. These ligands were coordinated with CrCl₃(THF)₃ to produce precatalysts **C1-C4** as green or blue powders (**Figure 1**)。.

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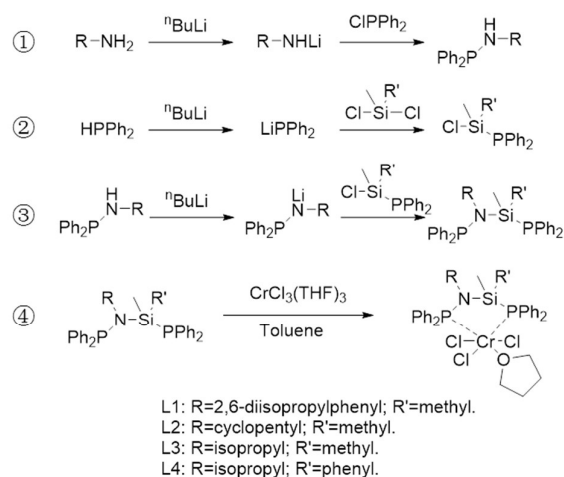
Figure 1. Synthesis and structures of the ligands and complexes.

L1: R=2,6-diisopropylphenyl; R'=methyl.
L2: R=cyclopentyl; R'=methyl.
L3: R=isopropyl; R'=methyl.
L4: R=isopropyl; R'=phenyl.

When activated by DMAO (dried methylaluminoxane, the methylaluminoxane was dried in vacuum at 60 °C for 2h)/AlEt$_3$

in methylcyclohexane, the precatalysts proved to be highly active and selective towards 1-hexene/1-octene (**Table 1**). **C1** was tested for ethylene oligomerization under 1 MPa of ethylene pressure (**Table 1**, entry 1) and showed 99% total selectivity (1-hexene+1-octene) and 6.4×10^6 g/(mol Cr·h) activity. It was believed that the sterically bulky N-substituted groups might be responsible for making such an effective catalyst. To modify the catalyst for ethylene tetramerization, we changed the N-substituted group from 2,6-diisopropylphenyl to cyclopentyl and isopropyl, obtaining **L2** and **L3**, respectively. When tested for ethylene oligomerization, the corresponding precatalysts **C2** and **C3** (**Table1**, entry 2 and entry 3) exhibited good performance, showing 60% selectivity toward 1-octene and 2.0×10^6 g/(mol Cr·h) oligomerization activities. Increasing the steric bulk on Si with phenyl substitution (**C4**) reversed the selectivity from tetramerization to trimerization (**Table1**, entry 4). Notably, profiting from the electronic effect, catalysts with aryl substituted groups on both the N and Si atoms show higher activities compared to those catalysts with only alkyl substituted groups.

Table 1. Comparison of the precatalysts for ethylene oligomerization.

Entry	Precatalyst	Activity (10^6 g/mol Cr·h)	Product selectivity (*wt* %)							
			C$_4$	C$_6$	1-C$_6^=$	^{a}C$_6'$	^{b}C$_6''$	C$_8$	1-C$_8^=$	≥1-C$_{10}^=$
1	C1	6.4	<1	89	99	trace	trace	10	98	<1
2	^{c}C2	2.2	1	38	72	4	6	61	98	trace
3	C3	1.8	1	38	79	3	5	61	97	trace
4	C4	4.9	<1	66	97	<1	1	33	97	trace

Reaction conditions: reaction temperature: 45 °C; reaction pressure:1.0 MPa; reaction time: 30 min; solvent: methylcyclohexane (20 mL); $n_{(cat)}$: 0.3μmol; $n_{(Al)}/n_{(Cr)}$=1000; DMAO:AlEt$_3$=4:1. ^{a}Methylcyclopentane in all products; ^{b}Methenecyclopentane in all products; $^c n_{(cat)}$: 0.6μmol;

C1 was further investigated for ethylene tri-/tetramerization under a set of reaction conditions that varied the temperature, ethylene pressure and precatalyst mass (**Table 2**). Higher temperature increased 1-hexene selectivity at the expense of 1-octene, but extremely high temperatures deactivated the catalyst and consequently lowered the activity (**Table 2**, entry 1-3). Reducing the precatalyst mass markedly promotes activity (**Table 2**, entry 2 and entry 4-5), which shows that large

masses of precatalyst prevent it from forming active species. This result is fully consistent with a spectral study reported by Do[32]. Although a low precatalyst mass efficiently converted into the active species, when the mass was reduced to 0.1 μmol, no activity was observed for ethylene oligomerization. However, increasing the $n_{(Al)}/n_{(Cr)}$ ratio from 500 to 10000 recovered its activity to 6.8×10^6 g/(mol Cr·h), with 78% selectivity towards 1-hexene (**Table 2**, entry 7).

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Table 2. Ethylene tetramerization by complex C1 under various conditions.

Entry	Ethylene pressure (MPa)	Precatalyst (μmol)	T (^{o}C)	Activity (10^6 g/mol Cr·h)	Product selectivity (wt %)							
					C_4	C_6	1-$C_6^=$	[a]C_6'	[b]C_6''	C_8	1-$C_8^=$	≥1-$C_{10}^=$
1	1	4.8	0	0.5	<1	60	99	<1	<1	39	98	<1
2	1	4.8	45	1.9	trace	86	99	trace	trace	5	96	9
3	1	4.8	60	1.6	trace	88	99	trace	trace	4	94	8
4	1	1.2	45	1.8	trace	86	>99	trace	trace	11	96	3
5	1	0.3	45	5.5	trace	88	>99	trace	trace	12	94	trace
6	1	0.1	45	[d]LA					Trace			
7	[c]1	0.1	45	6.8	trace	78	>99	trace	trace	22	95	Trace
8	[c]2	0.1	10	7.8	trace	74	>99	trace	trace	26	96	Trace
9	[c]4	0.1	10	16.8	trace	75	>99	trace	trace	25	97	Trace

Reaction conditions: reaction time, 30 min; solvent, methylcyclohexane (20 mL); $n_{(Al)}/n_{(Cr)}$=500; DMAO:AlEt$_3$=4:1. [a] Methylcyclopentane in all products; [b] Methenecyclopentane in all products; [c] $n_{(Al)}/n_{(Cr)}$=10000; [d] Low activity.

Combining a higher ethylene pressure with a low temperature can elevate the activity up to 16.8×10^6 g/(mol Cr·h) with the selectivities toward 1-hexene (75%) and 1-octene (24%), respectively. Aside from the ethylene dimer (C_4), it is notable that the cyclic C_6 byproducts, which were produced nearly in all ethylene tri-/tetramerization systems, were almost absent and the total selectivity of 1-hexene and 1-octene reached more than 99%. This high selectivity can be understood to occur via a plausible mechanism for trimerization (**Figure 2**). The expanded metallacyclic mechanism considers metallacycloheptane as a starting material, which undergoes β-H transfer by two different pathways. In one pathway, a 6, 2-H shift in (a), followed by a reductive elimination, converts intermediate (m) to 1-hexene (pathway A). Along the second pathway (pathway B), a C→M agostic H transfer allows two alternative pathways. After transferring β-H to the chromium center, a double bond forms between two carbon atoms to form a hexenyl chromium species (h), which eliminates 1-hexene via M→C agostic H transfer and performs decomplexation with the chromium center (pathway B'). Alternatively, β-H transfer to the chromium atom and a 2, 6-C bonding forms the key intermediate (d) for producing cyclic C_6

byproducts (pathway A'). Methyl and methylenecyclopentane formed according to our proposed LCrH(cyclopentylmethyl) mechanism[26] or LCrEt(cyclopentylmethyl) mechanism[33, 34]. The large distance between 2nd and 6th C decreases the chance of a 2, 6-C bonding, resulting in limited cyclic C_6 products, especially in ligands with a large steric bulk on N, such as the **L1** ligand.
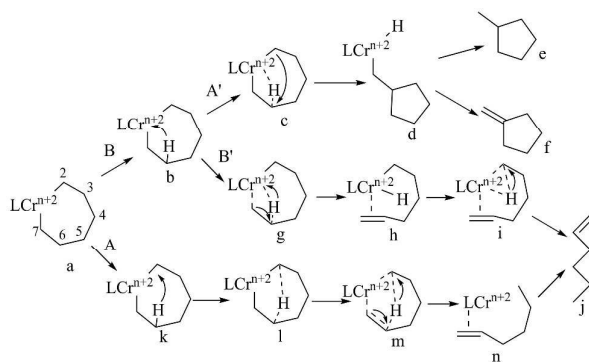

Figure 2. Mechanism of ethylene trimerization.

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Table 3. Ethylene tetramerization by complex C2 under various conditions.

Entry	Ethylene pressure (MPa)	Precatalyst (μmol)	T (^{o}C)	Activity (10^6 g/mol Cr·h)	Product selectivity (wt %)							
					C_4	C_6	$1\text{-}C_6^=$	$^a C_6'$	$^b C_6''$	C_8	$1\text{-}C_8^=$	$\geq 1\text{-}C_{10}^=$
1	1	4.8	45	0.7	1	41	80	3	5	58	97	Trace
2	1	1.2	45	1.5	1	42	77	4	6	57	99	Trace
^{c}3	1	0.6	45	2.2	1	38	72	4	6	61	98	Trace
^{d}4	1	0.1	45	8.9	2	37	74.0	3	6	61	99	Trace
^{e}5	1	0.3	10	0.7	3	27	33	8	13	70	97	Trace
^{e}6	1	0.3	45	4.1	1	38	76	4	6	61	99	Trace
^{e}7	1	0.3	60	0.2	2	48	90	<1	3	50	96	Trace
^{d}8	0.4	0.1	10	1.8	1	52	86	3	5	47	96	Trace
^{d}9	4	0.1	10	13.0	2	21	52	4	6	77	98	Trace

Reaction conditions: reaction time, 30 min; solvent, methylcyclohexane (20 mL); $n_{(Al)}/n_{(Cr)}$=500; DMAO:AlEt$_3$=4:1. ^{a} Methylcyclopentane in all products; ^{b} Methylenecyclopentane in all products; ^{c} $n_{(Al)}/n_{(Cr)}$=1000; ^{d} $n_{(Al)}/n_{(Cr)}$=6000; ^{e} $n_{(Al)}/n_{(Cr)}$=2000;

C2 was further investigated for ethylene tetramerization under various reaction conditions, and it was found that the results were consistent with the results of the **C1** precatalyst (**Table 3**). Here we also observed that the precatalyst mass played a significant role in catalyst activity (**Table 3**, entry 1-2) and only a small portion of the precatalyst became active species when a high concentration of precatalyst was present. Keeping the cocatalyst concentration constant, the catalytic activity increased significantly with a decreasing precatalyst concentration and reached up to 8.9×10^6 g/(mol Cr·h) (**Table 3**, entry 3-4). Low temperature and high ethylene pressure are benefit to **C2** for ethylene tetramerization, and selectivity was only slightly affected by the precatalyst mass. Under optimized conditions, **C2** produces 75% selective 1-octene and has 13.0×10^6 g/(mol Cr·h) oligomerization activity. Moreover, the cyclic byproducts dominated the C_6 products when less sterically hindered groups were attached to ligands.

The excellent activities and selectivities of these catalysts encouraged us to perform DFT calculations. The optimized structures of **C1** and **C2** (**Figure 3**) were selected as possible intermediates for a DFT study. The P-Cr-P bite angle is a very important factor in PNP and PCCP systems, and a small P-Cr-P bite angle is beneficial to 1-octene selectivity[35]. DFT calculations suggested that the different selectivities for these

two systems (**C1** and **C2**) might be due to their different P-Cr-P bite angles.

In a growing metallacycle, the P-Cr-P angle has to be decreased as much possible to decrease the steric constraint around the metal. The decreasing bite angles in intermediates from **C1a** to **C1c** and from **C2a** to **C2c** demonstrated this phenomenon. During this process, both the Cr-P-N-Si-P and Cr-C_n (n=4, 6 and 8) rings distorted due to the difference in the two Cr-C and two Cr-P bond distances, which allowed ring-opening decomposition to occur[22]. In the growing metallacycle, the two Cr-P bond distances changed very little from **C1a** to **C1b** and the Cr-P-N-Si-P ring remained stable enough to maintain the catalytic cycle. By contrast, the two P-Cr bond distances in **C1c** changed enough to decompose and deactivate the ring. Fortunately, the large steric bulk of the N-substituted group on **C1** distorted the metallacycloheptane and blocked further ethylene insertion. Thus, the metallacycloheptane efficiently released 1-hexene by reductive elimination and entered into the next catalytic cycle. In the case of **C2**, the two Cr-P bond distances remained similar for all of the cyclic intermediates, exhibiting good stability. The Cr-C bond distance in **C2b** was similar to that of **C1b** and it was less stable. The smaller steric bulk of the N-substituted group on **C2** facilitated further ethylene insertion,

which allowed the formation **C2c** and release of 1-octene by reductive elimination.
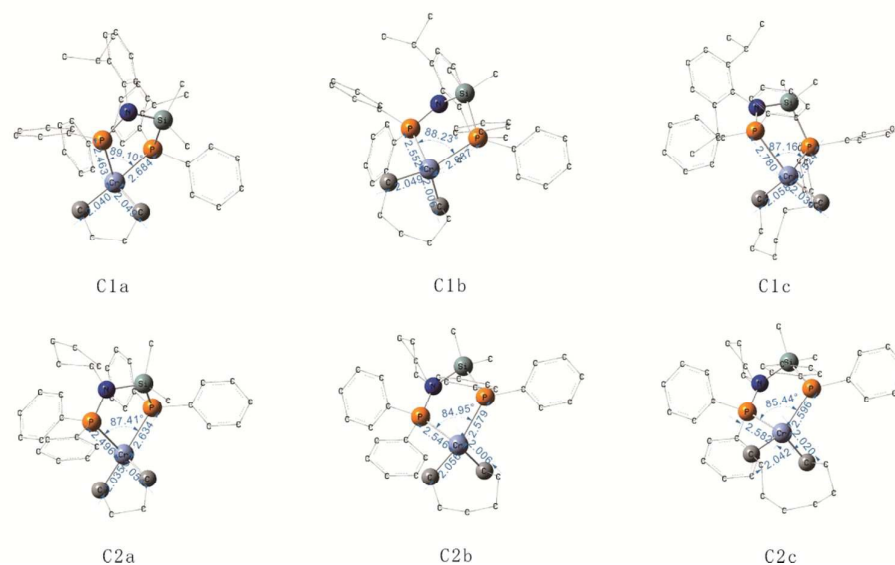

Figure 3. Optimized structures and main parameters of the possible reaction intermediates. (The unit of the bond length is Å; all of the spin multiplicities are quartets.).

Kinetic studies suggested that metallacycle growth is the rate-determining step[16, 36, 37] in ethylene oligomerization, according to the extended metallacyclic mechanism[6]. McGuinness et al.[38] further explored that the 1-hexene forms via ethylene coordination to a metallacyclopentane and the 1-octene forms via a dual pathway mechanism (via bis(ethylene) metallacyclopentane and via ethylene coordination to a metallacycloheptane). Hence, the tri- and tetramerization activity can be better explained by the coordination ability of the intermediates (metallacyclopentane for 1-hexene and metallacycloheptane for 1-octene) with ethylene, which is further related to the energy gaps between the intermediates' LUMOs and ethylene's HOMO.
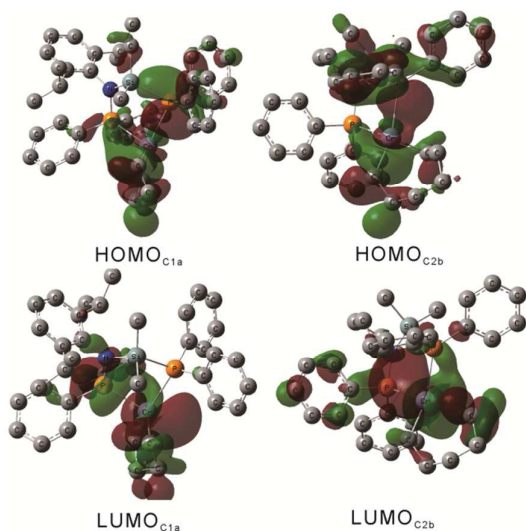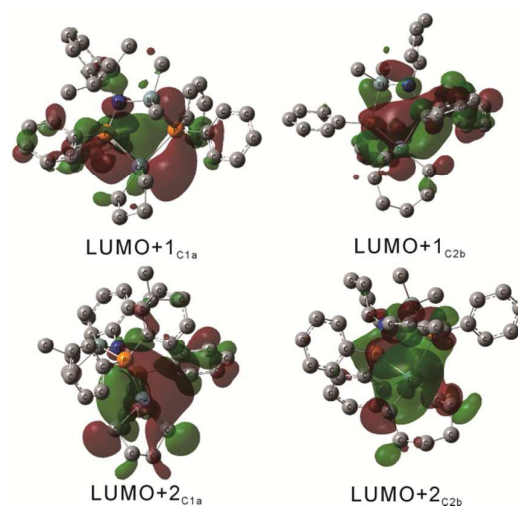

Figure 5. LUMO+1 (top) and LUMO+2 (bottom) of C1a and C2b.

To study the energy gaps (HOMOs/LUMOs) of ethylene and the intermediates, **C1a** and **C2b** were further investigated with molecular orbital (MO) energy calculations (shown in **Figure 4**). The HOMOs of both the **C1a** and **C2b** structures exhibit $3dz^2$ symmetry and thus have the capability to overlap with empty C_2H_4 π^* orbitals to form π back-bonding with an incoming ethylene molecule. Additionally, the geometric symmetry of empty 3d orbital preferentially accepts π electrons from the incoming ethylene. However, no well-matched orbitals (bottom row; **Figure 4**) were recognized and we further considered the LUMO+1 and LUMO+2 orbitals of the **C1a** and **C2b** structures (**Figure 5**). LUMO+1$_{C1a}$ and LUMO+1$_{C2b}$ appeared to be best suited for interacting with the corresponding HOMOs.

Figure 4. Frontier molecular orbitals of C1a and C2b. (top row: HOMO; bottom row: LUMO).

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As shown in **Table S1**, LUMO+1$_{C1a}$ is lower in energy than LUMO+1$_{C2b}$, and its corresponding energy gap (between LUMO+1$_{C1a}$ and HOMO$_{ethylene}$) is also less than LUMO+1$_{C2b}$ and HOMO$_{ethylene}$; therefore, **C1a** can coordinate with ethylene compared to **C2b** and give higher activity for ethylene oligomerization, which is consistent with our experimental results.

Conclusions

A series of silicon-bridged/N, P-based (SBNP) ancillary ligands were synthesized and characterized. The precatalysts obtained by the coordination of the ligands and CrCl$_3$(THF)$_3$ proved to be excellent catalysts for ethylene tri-/tetramerization when activated by DMAO/AlEt$_3$. **C1** and **C2** were observed to be the best catalysts, showing 16.8×10^6 g/(mol Cr·h) and 13.0×10^6 g/(mol Cr·h) activities for ethylene tri-/tetramerization, respectively. **C1** showed 99% total selectivities (75%, 1-hexene; 24%, 1-octene), while **C2** produced 75% selective 1-octene. The extremely low production of the cyclic C$_6$ byproducts was explained by a mechanism proposed for trimerization products. DFT calculations were also conducted to probe a theoretical base for the excellent activities and selectivities of these systems.

Experimental

General Procedure: All air and/or water sensitive reactions were performed under a nitrogen atmosphere in oven-dried flasks using standard Schlenk techniques or under a nitrogen atmosphere in a glovebox. Anhydrous reaction solvents were obtained by means of a multiple column purification system. Bis(phenyl)phosphorus chloride, Diphenylphosphine, dichlorodimethylsilane, n-butyllithium (2.4 mol/L in n-hexane) and CrCl$_3$(THF)$_3$ were purchased from Aldrich Chemical Co. (Milwaukee, WI, USA) and were used as received. Lithium diphenylphosphine was prepared using the method reported by Peterson[38]. Polymerization grade ethylene was obtained from Tianjin Summit Specialty Gases (China). Triethylaluminum (TEA, 1.0 mol/L in methylcyclohexane) and methylaluminoxane (MAO, 1.4 mol/L in toluene) were purchased from Albemarle Corp (USA). DMAO was prepared by pumping off all the volatile compounds of MAO at 40 °C for 6 h. NMR Spectroscopic data for the ligands were obtained using a Bruker Ultrashield 400 (400 MHz for ^{1}H, 162 MHz for ^{31}P and 100 MHz for ^{13}C in CDCl$_3$ or C$_6$D$_6$). Elemental analyses were performed by Chinese Academy of Sciences (Shanghai Institute of organic chemistry).

Ligand synthesis:

N-(2,6-diisopropylphenyl)-N-((diphenylphosphanyl)dimethylsilyl)-1,1-diphenylphosphanamine (L1): 8.3 mL of n-BuLi (2.4 mol/L in n-hexane, 19.92 mmol) was added dropwise at -20 °C to a solution of 2,6-diisopropylaniline (3.582 g, 20.00 mmol) in n-hexane (20 mL). The reaction mixture was stirred overnight at room temperature, followed by the addition of chlorodipenylphosphane (4.413 g, 20.00 mmol). The mixture was again stirred overnight at room temperature, the precipitated LiCl was filtered out, and the faint yellow solution was concentrated to give a yellow residue, which was recrystallized in hexane to give N-(2, 6- diisopropylpenyl)-1-dipenylphosphanamine (**L1a**) (4.92 g, 13.60 mmol) in 68% yield. n-BuLi (5.7 mL, 2.4 mol/L in n-hexane, 13.60 mmol) was added dropwise at -20°C to a solution of the above product. The mixture was stirred at room temperature for 5 h. After filtration and washing twice with 2 mL of n-hexane, lithium (2,6-diisopropylphenyl)(diphenylphosphanyl)amide (**L1b**) (4.997 g, 13.60 mmol,) was obtained in approximately 100% yield after drying in a vacuum. Lithium diphenylphosphanide (**L1c**) was prepared by a similar method to **L1b,** with diphenylphosphane (3.800 g, 20.00 mmol) and n-BuLi (8.3 mL, 19.92 mmol, 2.4 mol/L in n-hexane). A yellow solid (3.843 g, 20.00 mmol) was obtained in nearly 100% yield. The above yellow product was added portionwise to a solution of dichlorodimethylsilane (5.162 g, 40.00 mmol) in n-hexane (20 mL) at -20°C and then stirred at room temperature for 8 h. After filtration, the volatiles were removed in a vacuum, giving a yellow oil. The colorless oil (chlorodimethylsilyl)diphenylphosphane (**L1d**) was obtained by vacuum distillation (155°C~160°C, 10 mmHg, 2.137 g, 7.67 mmol, 38% yield). A solution of **L1d** (0.558 g, 2.00 mmol) in toluene (20 mL) was added dropwise to a solution of **L1c** (0.735 g, 2.00 mmol) in toluene (5 mL) at -20°C. After overnight stirring and filtration, a yellow oil was obtained by removing the volatiles in a vacuum. Recrystallization from n-hexane produced ligand **L1** (0.869, 1.44 mmol) in 72% yield. ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 7.98 (t, *J* = 7.5 Hz, 4H), 7.58 (dd, *J* = 10.4, 4.9 Hz, 4H), 7.14 − 6.96 (m, 15H), 3.58 − 3.46 (m, 2H), 1.11 (d, *J* = 6.7 Hz, 6H), 0.43 (d, *J* = 6.7 Hz, 6H), 0.41 (d, *J* = 2.0 Hz, 6H). ^{31}P NMR (162 MHz, C$_6$D$_6$) ^{31}P NMR (162 MHz, C$_6$D$_6$) δ 52.22 (d), -43.26 (d, *J*=25.9Hz). ^{13}C NMR (101 MHz, C$_6$D$_6$) δ 148.32, 142.44, 142.40, 139.06, 138.87, 137.71, 137.69, 137.53, 137.52, 136.13, 136.12, 136.09, 135.96, 135.91, 135.88, 135.85, 129.69, 128.90, 128.83, 128.61, 128.41, 128.16, 126.84, 125.12, 29.37, 29.34, 26.61, 26.60, 24.03, 2.71, 2.63, 2.56.

N-cyclopentyl-N-((diphenylphosphanyl)dimethylsilyl)-1,1-diphenylphosphanamine (L2): As for *L1a*, the preparation of N-cyclopentyl-1,1-diphenylphosphanamine (**L2a**) was achieved

by using cyclopentanamine (1.703 g, 20.00 mmol), n-BuLi (8.3 mL, 19.92 mmol, 2.4 mol/L in n-hexane) and chlorodiphenylphosphane (4.413 g, 20.00 mmol). Vacuum distillation at 10 mmHg gave the colorless oil **L2a** (150°C ~160°C, 2.811 g, 10.43 mmol, 52% yield). The preparation of **L2b** was conducted by the same method as described for **L1b** with n-BuLi (4.4 mL, 10.44 mmol, 2.4 mol/L in n-hexane) and **L2a** (0.551 g, 2.00 mmol) and was isolated in nearly 100% yield (2.871 g, 10.43 mmol). Similarly to **L1**, 0.685 g **L2** (1.34 mmol, 67% yield) was obtained by using **L2b** (0.551 g, 2.00 mmol) and **L1d** (0.558 g, 2.00 mmol). ^{1}H NMR (400 MHz, C_6D_6) δ 7.69 (t, 4H), 7.56 (t, 4H), 7.08 (m, 12H), 3.82 – 3.68 (m, 1H), 1.86 – 1.68 (m, 2H), 1.46 (m, 4H), 1.26 (m, 2H), 0.53 (s, 6H). ^{31}P NMR (162 MHz, C_6D_6) δ 51.96 (br), -53.72 (d, *J*=53.8Hz). ^{13}C NMR (101 MHz, C_6D_6) δ 140.90, 140.88, 140.70, 140.69, 137.30, 137.27, 137.12, 137.09, 135.49, 135.48, 135.31, 135.31, 133.08, 132.88, 128.86, 128.80, 128.74, 128.69, 128.42, 128.18, 63.09, 34.57, 34.55, 32.21, 23.79, 3.20, 3.08, 2.96.

N-((diphenylphosphanyl)dimethylsilyl)-N-isopropyl-1,1-diphenylphosphanamine (L3): N-isopropyl-1,1-diphenylphosphanamine (**L3a**) was synthesized by the method as **L1a** using isopropylamine (1.182 g, 20.00 mmol), n-BuLi (8.3 mL, 19.92 mmol, 2.4 mol/L in n-hexane) and chlorodiphenylphosphane (4.413 g, 20.00 mmol). Colorless oil **L3a** was obtained by vacuum distillation at 10 mmHg (140°C ~150°C, 2.628 g, 10.80 mmol, 54% yield). Similarly to **L1**, 0.631 g **L3** (1.30 mmol, 65% yield) was obtained by using **L3a** (0.487 g, 2.00 mmol), n-BuLi (0.8 mL, 1.92 mmol, 2.4 mol/L in n-hexane) and **L1d** (0.558 g, 2.00 mmol). ^{1}H NMR (400 MHz, C_6D_6) δ 7.95 – 7.72 (m, 4H), 7.46 – 7.36 (m, 2H), 7.32 – 7.25 (m, 2H), 7.18 (d, *J* = 16.4 Hz, 4H), 7.14 – 7.02 (m, 10H), 6.84 (s, 3H), 3.77 (td, *J* = 13.4, 6.4 Hz, 1H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.84 (s, 3H), 0.82 (s, 3H). ^{31}P NMR (162 MHz, C_6D_6) δ 52.08 (br), -57.15(d *J*=118.3Hz). ^{13}C NMR (101 MHz, C_6D_6) δ 140.77, 140.76, 140.58, 140.56, 140.55, 140.38, 140.35, 140.03, 139.99, 139.84, 139.79, 137.76, 137.58, 135.87, 135.82, 134.35, 134.20, 133.67, 133.46, 133.22, 133.02, 131.89, 131.69, 130.03, 129.00, 128.93, 128.85, 128.75, 128.68, 128.47, 128.42, 128.17, 127.13, 52.42, 25.84, 25.72, 0.27.

N-((diphenylphosphanyl)(methyl)(phenyl)silyl)-N-isopropyl-1,1-diphenylphosphanamine (L4):

(chloro(methyl)(phenyl)silyl)diphenylphosphane (**L4d**) was synthesized according to the method described for **L1d** by **L1c** (3.843 g, 20 mmol) and dichloro(methyl)(phenyl)silane (7.645 g, 40 mmol). Colorless oil **L4d** was yielded by vacuum distillation at 10 mmHg (165°C ~175°C, 3.136 g, 9.20 mmol, 46% yield). Similarly to **L1**, 0.767 g **L4** (1.40 mmol, 70% yield) was obtained by using **L3a** (0.487 g, 2.00 mmol), n-BuLi (0.8 mL, 1.92 mmol, 2.4 mol/L in n-hexane) and **L4d** (0.558 g, 2.00 mmol). ^{1}H NMR (400 MHz, C_6D_6) δ 7.73 – 7.64 (m, 4H), 7.59 – 7.49 (m, 4H), 7.15 – 7.00 (m, 12H), 3.75 (m, *J* = 13.4, 6.7 Hz, 1H), 1.08 (d, *J* = 6.7 Hz, 6H), 0.57 – 0.39 (m, 6H). ^{31}P NMR (162 MHz, C_6D_6) δ 50.42 (br), -53.03(d *J*=54.7Hz). ^{13}C NMR (101 MHz, C_6D_6) δ 140.71, 140.70, 140.52, 140.50, 137.28, 137.25, 137.10, 137.07, 135.55, 135.55, 135.38, 135.37, 133.22, 133.02, 128.84, 128.78, 128.70, 128.64, 128.42, 128.18, 52.27, 25.82, 25.79, 25.76, 3.49, 3.38, 3.26.

Precatalyst synthesis

[N-(2,6-diisopropylphenyl)-N-((diphenylphosphanyl)dimethylsilyl)-1,1-diphenylphosphanamine](THF)CrCl₃ (C1): A solution of **L1** (0.664 g, 1.10 mmol) was added dropwise to a solution of $CrCl_3(THF)_3$ (0.375 g, 1.00 mmol). A blue solution was obtained by stirring for 1 h. The resulting solution was added to 20 mL of n-hexane and then cooled at -30°C. Blue solid **C1** (0.609 g, 0.73 mmol, 78% yield) was obtained by filtration and dried in a vacuum. Anal. Calcd. for $C_{42}H_{51}Cl_3CrNOSiP_2$: C, 60.47; H, 6.16; N, 1.68. Found: C, 60.24; H, 6.21; N, 1.63.

[N-cyclopentyl-N-((diphenylphosphanyl)dimethylsilyl)-1,1-diphenylphosphanamine](THF)CrCl₃ (C2): **C2** was prepared with a yield of 81% by using the method for **C1** with **L2** (0.563 g, 1.10 mmol) and $CrCl_3(THF)_3$ (0.375 g, 1.00 mmol). Anal. Calcd. for $C_{35}H_{43}Cl_3CrNOSiP_2$: C, 56.65; H, 5.84; N, 1.89. Found: C, 56.92; H, 5.89; N, 1.82.

[N-((diphenylphosphanyl)dimethylsilyl)-N-isopropyl-1,1-diphenylphosphanamine](THF)CrCl₃ (C3): **C3** was prepared with a yield of 73% by using the method for **C1** with **L3** (0.534 g, 1.10 mmol) and $CrCl_3(THF)_3$ (0.375 g, 1.00 mmol). Anal. Calcd. for $C_{33}H_{41}Cl_3CrNOSiP_2$: C, 55.35; H, 5.77; N, 1.96. Found: C, 55.91; H, 5.67; N, 1.89.

[N-((diphenylphosphanyl)(methyl)(phenyl)silyl)-N-isopropyl-1,1-diphenylphosphanamine](THF)CrCl₃ (C4): **C4** was prepared with a yield of 69% by using the method for **C1** with **L4** (0.632 g, 1.10 mmol) and $CrCl_3(THF)_3$ (0.375 g, 1.00 mmol). Anal. Calcd. for $C_{38}H_{43}Cl_3CrNOSiP_2$: C, 58.65; H, 5.57; N, 1.80. Found: C, 58.87; H, 5.54; N, 1.78.

Ethylene Oligomerization: Ethylene oligomerization reactions were carried out in a 150 ml steel Büchi autoclave equipped with a mechanical stirrer and temperature probe. After catalyst injection into the autoclave under a stream of N_2, the autoclave was immediately pressurized with ethylene. The reaction was allowed to run for 30 min. The reactor was then quenched by cooling to 0 °C using an ice bath and depressurized. The products of oligomerization were analyzed by an Agilent 6890 gas chromatograph with a flame ionization detector (GC-FID) and an HP-5 GC capillary column. Heptane was used as the internal standard.

Computational details: All of the theoretical calculations were performed using the Gaussian 09 program package[40]. DFT was used to optimize the structures and to calculate those parameters using Becke-Lee-Yange-Parr functional (B3LYP) method. 6-31G (d, p) was used for the atoms of C, H, N, Si and P, while Cr was described with the LANL2DZ (ECP) basis set[41-43]. The Gaussian View 5.0 program was used to build the structures and produce the LUMOs and HOMOs. Monovalent cations with quartet spin states were considered in theoretical models for the DFT study[29, 41, 44-46].

Supporting Information

^{1}H NMR, ^{31}P NMR and ^{13}C NMR spectrums of **L1-L4** and absolute energies of all intermediates (PDF)
Cartesian coordinates for all intermediates (XYZ)

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Author Contributions

The manuscript was written through contributions of all of the authors. All of the authors have given approval to the final version of the manuscript.

Conflicts of interest
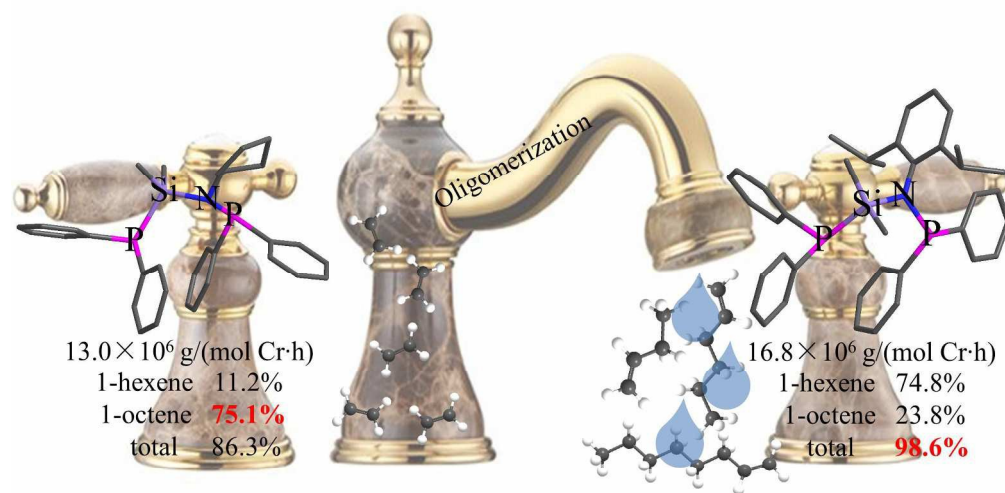
There are no conflicts to declare.

References

1. A. Bollmann, K. Blann, J. T. Dixon, F. M. Hess, E. Killian, H. Maumela, D. S. McGuinness, D. H. Morgan, A. Neveling and S. Otto, *Journal of the American Chemical Society*, 2004, **126**, 14712-14713.
2. G. Belov, *Petroleum Chemistry*, 2012, **52**, 139-154.
3. T. Agapie, *Coord. Chem. Rev.*, 2011, **255**, 861-880.
4. P. W. Van Leeuwen, N. D. Clément and M. J.-L. Tschan, *Coord. Chem. Rev.*, 2011, **255**, 1499-1517.
5. K. Alferov, I. Babenko and G. Belov, *Petroleum Chemistry*, 2017, **57**, 1-30.
6. M. J. Overett, K. Blann, A. Bollmann, J. T. Dixon, D. Haasbroek, E. Killian, H. Maumela, D. S. McGuinness and D. H. Morgan, *J. Am. Chem. Soc.*, 2005, **127**, 10723-10730.
7. P. R. Elowe, C. McCann, P. G. Pringle, S. K. Spitzmesser and J. E. Bercaw, *Organometallics*, 2006, **25**, 5255-5260.
8. S. Kuhlmann, K. Blann, A. Bollmann, J. T. Dixon, E. Killian, M. C. Maumela, H. Maumela, D. H. Morgan, M. Prétorius and N. Taccardi, *Journal of catalysis*, 2007, **245**, 279-284.
9. E. Killian, K. Blann, A. Bollmann, J. T. Dixon, S. Kuhlmann, M. C. Maumela, H. Maumela, D. H. Morgan, P. Nongodlwana and M. J. Overett, *Journal of Molecular Catalysis A: Chemical*, 2007, **270**, 214-218.
10. K. Blann, A. Bollmann, H. de Bod, J. T. Dixon, E. Killian, P. Nongodlwana, M. C. Maumela, H. Maumela, A. E. McConnell and D. H. Morgan, *J. Catal.*, 2007, **249**, 244-249.
11. Z. Weng, S. Teo and T. A. Hor, *Dalton Transactions*, 2007, 3493-3498.
12. T. Jiang, S. Zhang, X. Jiang, C. Yang, B. Niu and Y. Ning, *J. Mol. Catal. A: Chem.*, 2008, **279**, 90-93.
13. T. E. Stennett, T. W. Hey, L. T. Ball, S. R. Flynn, J. E. Radcliffe, C. L. McMullin, R. L. Wingad and D. F. Wass, *ChemCatChem*, 2013, **5**, 2946-2954.
14. S. Sa, S. M. Lee and S. Y. Kim, *Journal of Molecular Catalysis A: Chemical*, 2013, **378**, 17-21.
15. T. Jiang, H. X. Chen, Y. N. Ning and W. Chen, *Chin. Chem. Lett.*, 2006, **17**, 358.
16. D. S. McGuinness, D. B. Brown, R. P. Tooze, F. M. Hess, J. T. Dixon and A. M. Slawin, *Organometallics*, 2006, **25**, 3605-3610.
17. M. J. Overett, K. Blann, A. Bollmann, R. de Villiers, J. T. Dixon, E. Killian, M. C. Maumela, H. Maumela, D. S. McGuinness and D. H. Morgan, *Journal of Molecular Catalysis A: Chemical*, 2008, **283**, 114-119.
18. C. Klemps, E. Payet, L. Magna, L. Saussine, X. F. Le Goff and P. Le Floch, *Chemistry–A European Journal*, 2009, **15**, 8259-8268.
19. A. Dulai, C. L. McMullin, K. Tenza and D. F. Wass, *Organometallics*, 2011, **30**, 935-941.
20. T. Jiang, Y. Tao, X. Gao, G. Mao, H. Chen, C. Cao and Y. Ning, *Chin. Sci. Bull.*, 2012, **57**, 1510-1515.
21. Y. Shaikh, K. Albahily, M. Sutcliffe, V. Fomitcheva, S. Gambarotta, I. Korobkov and R. Duchateau, *Angewandte Chemie International Edition*, 2012, **51**, 1366-1369.
22. S.-K. Kim, T.-J. Kim, J.-H. Chung, T.-K. Hahn, S.-S. Chae, H.-S. Lee, M. Cheong and S. O. Kang, *Organometallics*, 2010, **29**, 5805-5811.
23. T. Jiang, Y. Ning, B. Zhang, J. Li, G. Wang, J. Yi and Q. Huang, *J. Mol. Catal. A: Chem.*, 2006, **259**, 161-165.
24. G. Mao, Y. Ning, W. Hu, S. Li, X. Song, B. Niu and T. Jiang, *Chinese Science Bulletin*, 2008, **53**, 3511-3515.
25. D. S. McGuinness, P. Wasserscheid, W. Keim, D. Morgan, J. T. Dixon, A. Bollmann, H. Maumela, F. Hess and U. Englert, *J. Am. Chem. Soc.*, 2003, **125**, 5272-5273.
26. L. Zhang, X. Meng, Y. Chen, C. Cao and T. Jiang, *ChemCatChem*, 2017, **9**, 76-79.
27. S. Härzschel, F. E. Kühn, A. Wöhl, W. Müller, M. H. Al-Hazmi, A. M. Alqahtani, B. H. Müller, N. Peulecke and U. Rosenthal, *Catal. Sci. Technol.*, 2015, **5**, 1678-1682.
28. K. Albahily, S. Licciulli, S. Gambarotta, I. Korobkov, R. Chevalier, K. Schuhen and R. Duchateau, *Organometallics*, 2011, **30**, 3346-3352.
29. K. Albahily, V. Fomitcheva, S. Gambarotta, I. Korobkov, M. Murugesu and S. I. Gorelsky, *J. Am. Chem. Soc.*, 2011, **133**, 6380-6387.
30. O. L. Sydora, T. C. Jones, B. L. Small, A. J. Nett, A. A. Fischer and M. J. Carney, *ACS Catalysis*, 2012, **2**, 2452-2455.
31. Y. Yang, Z. Liu, B. Liu and R. Duchateau, *ACS Catalysis*, 2013, **3**, 2353-2361.
32. L. H. Do, J. A. Labinger and J. E. Bercaw, *ACS catalysis*, 2013, **3**, 2582-2585.
33. G. J. Britovsek, D. S. McGuinness, T. Wierenga, C. Young. *ACS Catalysis*, 2015, 5(7), 4152-4166.
34. P. H. Budzelaar. J. Chem. 2009, 87 (7), 832-837.
35. J. Zhang, X. Wang, X. Zhang, W. Wu, G. Zhang, S. Xu and M. Shi, *ACS Catalysis*, 2013, **3**, 2311-2317.
36. R. Manyik, W. Walker and T. Wilson, *J. Catal.*, 1977, **47**, 197-209.
37. Y. Yang, H. Kim, J. Lee, H. Paik and H. G. Jang, *Applied Catalysis A: General*, 2000, **193**, 29-38.
38. G. J. Britovsek, D. S. McGuinness and A. K. Tomov, *Catalysis Science & Technology*, 2016, **6**, 8234-8241.
39. D. J. Peterson, *J. Organomet. Chem.*, 1967, **8**, 199-208.
40. M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci and G. Petersson, *See the Supporting Information for full reference*, 2013.
41. M. Gong, Z. Liu, Y. Li, Y. Ma, Q. Sun, J. Zhang and B. Liu, *Organometallics*, 2016.
42. T. J. De Bruin, L. Magna, P. Raybaud and H. Toulhoat, *Organometallics*, 2003, **22**, 3404-3413.
43. F. A. Pasha, J.-M. Basset, H. Toulhoat and T. de Bruin, *Organometallics*, 2015, **34**, 426-431.
44. Y. Yang, Z. Liu, L. Zhong, P. Qiu, Q. Dong, R. Cheng, J. Vanderbilt and B. Liu, *Organometallics*, 2011, **30**, 5297-5302.
45. Y. Yang, Z. Liu, R. Cheng, X. He and B. Liu, *Organometallics*, 2014, **33**, 2599-2607.

46. K. Albahily, Y. Shaikh, E. Sebastiao, S. Gambarotta, I. Korobkov and S. I. Gorelsky, *J. Am. Chem. Soc.*, 2011, **133**, 6388-6395.

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