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Chromium(III) catalysts based on tridentate silicon-bridged tris (diphenylphosphine) ligands for selective ethylene tri-/tetramerization



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ABSTRACT

The chromium(III) catalysts based on tridentate silicon-bridged tris(diphenylphosphine) ligands of the form $RSi(CH_2PPh_2)_3$ (L¹: R = Me; L²: R = Cy; L³: R = Ph) were investigated for selective ethylene tri-/ tetramerization. The steric and electronic properties of the substituents attached to the silicon moiety have been observed to have a great impact on the catalytic performance of these catalysts. Singlecrystal analysis, high-resolution mass spectrometry (HR-MS), and elemental analysis revealed that these complexes may adopt mononuclear tridentate coordination mode (k^3 -P, P, P) with Cr center. However, one of the phosphorus atoms in these complexes may act as a hemilabile donor and presumably loses its coordination with chromium in the presence of a competent donor which consequently transformed the tridentate complexes to bidentate (k^2 -P, P) coordination mode. Backbone modification of L¹ of the precatalyst **1** via successive abstraction of methylene spacers may offer $MeSi(CH_2)_n(PPh_2)_3$ (L⁴: n = 2; L⁵: n = 1; L⁶: n = 0) type chromium(III) complexes. Ethylene oligomerization of these systems suggested that the methylene spacers may effectively tune the complex structure and catalytic performance. Precatalyst 1 and 4 respectively based on L^1 and L^4 deliver 70% C₈ selectivity in the liquid oligometric fraction and considerable activity under experimental conditions. DFT investigations based on catalyst 4 revealed that the catalyst may simultaneously facilitate the single and double coordination pathways for C₈ formation, however, the single coordination pathway is thermodynamically more favorable for this system.

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1. Introduction

Over recent decades, selective oligomerization of ethylene toward α -olefins continuous to be an active research field in both industry and academia [1]. Linear α -olefins (LAOs), particularly 1-hexene and 1-octene are extensively used as comonomers in the production of linear low-density polyethylene (LLDPE) and consequently gained over-weighted demand [2]. To meet the market need and to avoid the less valuable fractions, often offered by conventional facilities, selective production of 1-hexene and 1-octene is therefore highly desirable [1c,3].

Although, the current knowledge relies on that the selective ethylene oligomerization follows the metallacycle mechanism in which an active metal (mostly chromium) facilitates a particular

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oxidation state to the metallacycle intermediates, which then liberate selective products [4]. However, the paramagnetic behavior of chromium and the unidentified nature of the redox couple of the catalyst system may impede to explore the mechanistic realm completely [5].

Ligand plays a crucial role in stabilizing a particular oxidation state of the catalyst and thus govern the selectivity. The modification of a ligand scaffold can, therefore, be used as a tool for tuning the product selectivity [5b,6]. A slight modification in the PNP trimerization system to establish a selective tetramerization system is an excellent example of selectivity tuning [4c,7]. Further investigations revealed that steric hindrance and pendant donor coordination of ligands are the other well-established factors that can mediate the tri- and tetramerization switching [8]. Despite the huge assortment, the tetramerization selectivity is still far from the level of trimerization systems [4c,10]. The exceptional performance of the trimerization systems was attributed to the ligands deprotonation during the catalytic cycle



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[9], however, the high 1-hexene selectivity offered by neutral ligands made this speculation ambiguous [10]. One possible reason for the low performance of the oligomerization systems is the poor stability of the complexes. In contrast to efficient trimerization systems in which the ligands are tris-ligated with chromium and offered stable catalysts, the tetramerization systems are bidentate and may comparatively exhibit less stability. Spectroscopic investigations suggested that the abstraction of the ligand from the chromium center seems quite possible, especially when treated with MAO or AlMe₃ [9a,11]. In this scenario, the exploring of the selective tetramerization systems based on tridentate ligands may prove very effective (the tridenticity may provide extra stability to catalyst) [12] and may establish the high selective 1octene systems comparable to that of high efficient trimerization systems. Moreover, the third donor may also act as a hemilabile donor and may also enhance the catalytic performance toward selective ethylene tetramerization [8d].

We previously found that Cr catalysts based on silicon-bridged ligands offered efficient catalytic systems for selective ethylene tri-/tetramerization. The silicon moiety in the ligand scaffold may not only influence the complex structure but also considerably alters the catalytic performance toward ethylene oligomerization [13]. The Cr complexes of silicon-based PNP [14], PNS [15], PCP [16], and NP [17] ligands provided as much as 320 kg(product). $g(Cr)^{-1} \cdot h^{-1}$ high catalytic activity (in case of silicon-bridged NP ligands) [17] and 83% C8 selectivity (in case of silylated-PNP ligands) [14]. Addressing the ligand stability and tuning the steric environment of the catalyst, here we aimed to design the Cr(III) catalysts based on tridentate silicon-bridged tris(diphenylphosphine) ligands and investigate its performance toward C₈ selectivity. The Cr(III) catalysts 1-6 were prepared and scrutinized for selective ethylene oligomerization. Upon activation with DMAO/ AlEt₃, the targeted catalysts deliver more than 70% C₈ selectivity in the liquid oligomeric fraction and considerable activity under experimental conditions. The catalyst environment has also been tailored by the successive abstraction of the methylene spacers in the ligand framework and explored the role of the methylene spacers as well as the effect of steric bulk at silicon moiety in the ligand scaffold. Moreover, DFT calculations were performed to explore the mechanistic aspects and to rationalize the 1-C₈ selectivity offered by these complexes.

2. Experimental

2.1. General comments

All procedures were carried out in oven-dried glassware under N₂ atmosphere using standard Schlenk technique or purified N₂-filled glove box. Anhydrous solvents were obtained using a multi-column purification system, while all the reagents were purchased from Aldrich and used as received. NMR spectra were recorded by Bruker Ascend^{III}-400 (400 MHz for ¹H, 162 MHz for ³¹P and 101 MHz for ¹³C in CDCl₃) at 300 K. Elemental analysis was performed on an Elemental Vario EL analyzer. High-resolution mass spectrometry (HR-MS) data were obtained on an LCMS-IT-TOF (SHIMADZU).

2.2. Ligand synthesis and catalyst preparation: general procedure

The silicon-bridged tris(diphenylphosphine) L^1-L^3 ligands of the form **RSi(CH₂PPh₂)₃** were prepared via a simple salt metathesis method. The methyldiphenylphosphine (Ph₂PCH₃), when reacted with n-butyllithium in the presence of tetramethylethylenediamine (TMEDA), affords Ph₂PCH₂Li.TMEDA complex which upon reacting with the corresponding trichlorosilane reagents may

produce the corresponding $L^{1}-L^{3}$ ligands. The $L^{1}-L^{3}$ ligands were then coordinated with $CrCl_{3}(THF)_{3}$ in $CH_{2}Cl_{2}$ solvent to produce the corresponding 1-3 complexes (Scheme 1). The progressive abstraction of methylene spacers in L^{1} may successfully provide the **MeSi(CH_2)n(PPh_2)_{3}**-type $L^{4}-L^{6}$ ligands. Treatment of diphenylphosphine with n-butyllithium may afford the lithium diphenylphosphanide (Ph_2PLi) salt which upon reacting with the corresponding $L^{4}-L^{6}$ ligands. The $L^{4}-L^{6}$ were then coordinated with $CrCl_{3}(THF)_{3}$ in $CH_{2}Cl_{2}$ solvent to obtained the corresponding 4-6complexes (Scheme 2). The detailed synthesis procedures of $L^{1}-L^{6}$ ligands and their corresponding 1-6 complexes have been illustrated in Supporting Information.

2.3. Ethylene oligomerization

Transparent glass (for 1.0 MPa pressure) or stainless steel (for 4.0 MPa pressure) autoclave reactor (150 mL) equipped with a stirrer and temperature probing device was used for selective ethylene oligomerization. Under N₂ atmosphere, the catalyst was injected into the reactor followed by pressurized ethylene and run the reaction for 30 min. After completion of the reaction, the reactor was cooled to -15 °C temperature and the oligomerization was quenched by releasing pressure and using acidified MeOH (50 mL). The organic phase was separated and analyzed by GC-FID (gas chromatography with flame ionization detector) using Agilent 6890 with HP-5 GC capillary column, while heptane was used as an internal standard.

3. Results and discussion

To explore the role of backbone Si-substituents in controlling activity and selectivity, Cr precatalysts 1-3 were subjected to oligomerization testing. Under 1.0 MPa ethylene pressure in methylcyclohexane (MeCy) solvent and in the presence of DMAO/AlEt₃ cocatalyst, the precatalyst **1** affords 60% C₈ selectivity with considerable activity (Table 1, entry 1). Increasing the steric bulk of the backbone silyl-substituent by the replacement of the methyl group (in 1) with a cyclohexyl group (in 2) preserved the catalytic activity under experimental conditions, however, considerably decrease the C_8 selectivity (Table 1, entry 2) [4c,18]. Moreover, the substitution of the phenyl group at Si (in **3**) may not only diminish the C₈ selectivity but also significantly reduces the catalytic activity (Table 1, entry 3). Furthermore, the precatalyst **3** also produces a considerable amount of C₄ fraction and may offer a wide distribution of oligomers. These results suggested that not only the steric bulk of Si moiety but also the electronic properties considerably influence the catalytic performance in these systems [19].

To our knowledge, the formation of C_8 fraction with 60% selectivity by tris-ligated Cr complexes is the first example that we observed here. These results encouraged us to scrutinize other ligands of the same series for selective ethylene tetramerization.

To investigate the role of methylene spacers of the ligand scaffold in tuning the catalyst performance, the precatalysts **4–6** have been scrutinized for ethylene oligomerization. Upon screening, the precatalyst **4** showed an improved selectivity of 68% toward C₈ fraction under comparable conditions (Table 1, entry 4). The methylene abstraction in precatalyst **4** may tailor the steric environment of the active catalyst and stabilize the chromacyclononane intermediate, consequently release more C₈ [20]. Further methylene abstraction as in **L⁵-L⁶** may lead the corresponding precatalysts **5–6** to less active and less selective systems (Table 1, entries 5–6). The precatalyst **6** with no methylene spacer may produce a considerable amount of C₄ and C₆ products at the



Scheme 1. Synthesis of L¹-L³ and corresponding Cr 1–3 complexes.







4: $n_1 = n_2 = 1$, $n_3 = 0$ 5: $n_1 = 1$, $n_2 = n_3 = 0$ 6: $n_1 = n_2 = n_3 = 0$

Scheme 2. Synthesis of L⁴-L⁶ and corresponding Cr **4**–**6** complexes.

expense of C_8 fraction with attenuated activity. These results suggested that not only the steric and electronic properties of the Si group but also the methylene spacers of the ligand backbone can

tune the catalytic performance. The overall low catalytic activity of **1–6** complexes could be attributed to low stability and low solubility of these catalysts in the MeCy solvent [21,22].

Table 1				
Ethylene oligomerization	with Cr(III) tridentate	silicon-bridged	tris(diphenylphosphi	ne) 1-6 complexes. ^a

			Product sel				
Entry	Precatalyst	Activity ^b	C4 ^c	C ₆ ^c	1-C ₆	C ₈ ^{c, d}	PE (g)
1	1	1121	2	37	51	60	0.17
2	2	1311	2	32	84	46	0.10
3	3	165	10	32	>99	35	0.15
4	4	1329	1	25	48	68	0.24
5	5	1075	4	39	59	47	0.29
6	6	147	18	50	>99	30	0.22

^a General conditions: *n*(precatalyst), 2.4 μmol; pressure, 1.0 MPa; solvent, methylcyclohexane (20 mL); reaction time, 30 min; *T*, 15 °C; *n*(Al)/*n*(Cr), 500 equiv; *n*(DMAO)/*n* (AlEt₃), 4:1.

^b g(product) $g(Cr)^{-1}h^{-1}$.

^c wt % of liquid products (oligomers).

^d C₈ contains 100% 1-C₈.

Although the catalytic activity and C_8 selectivity of tridentate silicon-bridged tris(diphenylphosphine) based Cr(III) **1–6** complexes are lower than the state of the art catalysts [4c,23], however, the formation of 60% C_8 product with tridentate Cr(III) catalysts is intriguing and encouraging. Besides the liquid oligomeric products, the oligomerization mixture also consists of a considerable amount of solid polymer. The formation of polymer in almost all catalytic runs suggested that in addition to active catalyst an independent polymerization catalyst also present in the system [24].

The chromium precursors in ethylene trimerization catalysts mostly coordinated with tridentate ligands in a *facial* or *meridional* fashion, whilst, tetramerization catalysts mostly exhibited bidentate coordination mode [2,25]. To explore the coordination chemistry and thus to explicate the role of tridenticity in controlling the catalytic performance of tridentate silicon-bridged tris (diphenylphosphine) based Cr complexes, the L¹ based Cr(CO)₃ complex was selected for single-crystal X-ray diffraction analysis. The reaction of L¹ with Cr(CO)₆ in refluxing toluene turns the colorless solution to pale yellow, demonstrating the complex formation. Upon recrystallization from CH₂Cl₂/hexane, L¹/Cr(CO)₆ solution provides the desired [Cr(CO)₃(k^3 -P, P, P-L¹) complex **7** (Scheme 3), the structure of complex **7** is illustrated in Fig. 1.

For complex **7**, XRD confirmed the expected octahedral geometry of the product as a six-coordinated Cr complex, where the ligand coordinated with Cr via phosphorus donors in a $fac-k^3$ -P, P, P tridentate mode. The complex exhibits threefold symmetry with the threefold axis along with the C–Si–Cr core having equivalent arms (Fig. 1). Although the complex **7** is a neutral specie with Cr(0) center and may be different from the Cr(III) complexes, however, for structural elucidation of Cr(III) complexes the Cr(0) complexes can also be used [8a,14,26]. Moreover, the Cr(0) complexes could be converted to cationic active species by using suitable activator (oxidizing agent) which can then exhibit comparable catalytic activity and product selectivity to that of Cr(III) catalysts under similar conditions [27].

In attempts to get the single crystals of Cr(III) complexes, we only succeeded in obtaining the single crystals of complex **2** from







Fig. 1. ORTEP (ellipsoids as 50%) diagram of Cr(CO)₃-**L**¹ (7); H atoms are omitted for clarity. Symmetry-related atoms are labelled once. Selected bond lengths (Å): Cr1–P1, 2.4129(8); Cr1–C1, 1.835(3); Si1–C14, 1.883(3); Si1–C15, 1.860(5); P1–C14, 1.838 (3); P1–C2, 1.830(3); P1–C8, 1.849(3); O1–C1, 1.161(3). Selected bond angles (deg): P1–Cr–P1, 89.89(3); C14–Si1–C14, 108.29(9); C15–Sil–C14, 110.63(9); O1–C1–C1–(1, 172.6(2).

the THF/hexane solvent system. Although, this result confirmed the mononuclear coordination of L^2 with Cr(III), however, in contrast to complex 7, in which the L^1 is coordinated with Cr(0) in a tridentate binding mode, the L^2 in Cr(III) complex 2 coordinated in a bidentate $[CrCl_3(THF)(k^2-P, P-L^2)]$ binding mode (Fig. 2). To further assess the complex structure and coordination of Cr(III) complexes, additional spectroscopic measurements (elemental analysis and HR-MS) have been performed. In contrast to the single-crystal result of CrCl₃(THF)-L², the elemental analysis, and HR-MS measurements (see Supporting Information) both support the mononuclear tridentate coordination of complex 2 with no coordination of THF molecule. Gardner et al. also reported Cr(III) complexes of similar ligands with mononuclear tridentate coordination mode albeit with smaller dialkylphsophines [12b]. Based on these results it is conceived that one of the phosphorus atoms in these Cr(III) 1-6 complexes may have weak coordination with chromium center, and may act as a hemilabile donor that can be replaced by the coordinating solvent molecules like THF which behave as a competent donor during the single crystal formation process [8a]. Furthermore, the temporary loss of one phosphorus coordination with Cr center of complex 4 during double ethylene coordination in the exploration of Gibbs



Fig. 2. ORTEP (ellipsoids as 50%) diagram of CrCl₃(THF)-L²; H atoms are omitted for clarity. Selected bond lengths (Å): Cr1–P1, 2.541(1); Cr1–P2, 2.475(1); Cr1–O1, 2.075(3); Cr1–Cl2, 2.315(1); Cr1–Cl3, 2.296(1); Cr1–Cl4, 2.302(1).). Selected bond angles (deg): P1–Cr1–P2, 89.13(4); P1–Cr1–O1, 89.32(8); P2–Cr1–O1, 176.65(9); C^{Ph}–P1–Cr1 (average), 116.40; C^{Ph}–P2–Cr1 (average), 116.75.

free energy profiles also validates the hemilabile nature of phosphorus atom (Fig. 3).

Oligomerization screening at low ethylene pressure has been performed for 1-6 complexes at different experimental conditions (Table 2). The high selective tetramerization complexes (1 and 4) exhibit high C₈ selectivity at low temperatures and a comparative high catalyst loading (Table 2, entries 2 and 19). Low temperature may favor the chain propagation towards chromacyclononane rather than reductive elimination of chromacycloheptane and consequently produce more C₈. Moreover, high ethylene concentration at low temperatures may also enhance the formation of the C₈ product [28]. The catalyst systems based on precatalysts 2-3 fail to produce high C₈ selectivity and may promote C₆ selectivity (Table 2, entries 7–17). As discussed prior, the low C_8 selectivity of 2-3 could be attributed to the steric and electronic properties of the silvl moiety, which may hinder the ethylene coordination with the catalytic active center to promote tetramerization [4c.29]. Precatalyst 5 based system may behave as a mixed tri-/ tetramerization catalyst and offer 65% C₆ (Table 2, entry 28) and 52% C_8 (Table 2, entry 29) selectivity at suitable conditions. The switching of C_6 and C_8 selectivity in precatalyst 5 shows that experimental conditions may shift the equilibrium between different active species which responsible for the formation of different selective products [24,30]. The precatalyst 6 based system having no methylene spacer mostly display C_6 selectivity at all experimental conditions (Table 2, entries 30-34) that become more pronounced at high temperature (Table 2, entry 33) [4c,14]. All the 1-6 precatalysts displayed high C_6 selectivity at elevated temperature which shows that high temperature may promote the formation of C_6 products at the expense of C_8 fraction (Table 2, entries 5, 16, 23, 28, and 33) [28a, 31].



Fig. 3. Free energy profiles for ethylene oligomerization catalyzed by catalyst 4 (⁶1); All stationary points are cationic.

Table 2

Evaluation of **1–6** complexes for ethylene oligomerization at different reaction conditions.^a

		Activity ^b	Product sel	Product selectivity (wt %)				
Entry Precatalyst	Precatalyst		C4 ^c	C ₆ ^c	1-C ₆	C ₈ ^{c,k}	PE (g)	
1	1	6385	1	45	80	49	0.16	
2 ^{d, f}		1121	2	37	51	60	0.17	
3 ^{d,j}		87	1	40	>99	26	0.02	
4 ^{e,j}		128	7	49	41	43	0.06	
5 ^g		3846	1	55	87	37	0.11	
6 ⁱ		7058	1	41	76	54	0.11	
7	2	1523	3	70	87	16	0.03	
8 ^{d,f}		1311	2	32	84	46	0.10	
9 ^{d,j}		66	1	54	57	43	0.03	
10 ^{e,j}		313	18	82	>99	0	0	
11 ^g		503	9	50	92	40	tr	
12 ⁱ		1523	4	73	67	21	0.02	
13	3	748	5	49	90	36	0.12	
14 ^{d,f}		165	10	32	>99	35	0.15	
15 ^{d,h}		250	11	57	61	18	0.10	
16 ^g		815	8	66	77	16	0.09	
17 ⁱ		958	7	50	72	35	0.09	
18	4	4654	1	42	86	52	0.17	
19 ^{d,f}		1329	1	25	48	68	0.24	
20 ^{d,h}		2500	1	41	78	52	0.21	
21 ^{<i>d</i>} j		83	3	43	63	17	0.27	
22 ^{e,j}		148	25	40	>99	33	0.12	
23 ^g		6577	1	58	86	36	0.14	
24 ¹		8288	1	37	78	59	0.11	
25	5	1713	0	50	78	45	0.15	
26 ^{d,r}		1075	4	39	59	47	0.29	
27 ^{d,n}		742	5	56	71	38	0.14	
28 ^g		1961	4	65	88	30	0.10	
29 ¹		3288	2	44	75	52	0.11	
30	6	1179	6	61	62	32	0.17	
31 ^{4,1}		147	18	50	>99	30	0.22	
32 ^{u,ii}		681	6	55	60	32	0.15	
33 ^s		1769	5	64	75	30	0.13	
34 ¹		1142	8	61	60	30	0.10	

^a General conditions: *n*(precatalyst), 1.2 μmol; pressure, 1.0 MPa; solvent, methylcyclohexane (20 mL); reaction time, 30 min; *T*, 45 °C; *n*(Al)/*n*(Cr), 500 equiv; *n*(DMAO)/*n* (AlEt₃), 4:1.

^b g(product)·g(Cr)⁻¹·h⁻¹.

^c wt % of liquid products (oligomers).

^d n(precatalyst), 2.4 μmol.

^e toluene.

^f *T*, 15 °C.

^g T, 60 °C.

^h n(Al)/n(Cr), 250 equiv.

ⁱ *n*(Al)/*n*(Cr), 1000 equiv.

^j MAO.

^k C_8 contains 100% 1- C_8 . tr = traces.

Low Al/Cr ratio, low reaction temperature coupled with high catalyst loading dramatically reduce the activities of all the 1-6 complexes (Table 2, entries 2, 8, 14-15, 19-20, 26-27 and 31-32) and could be attributed to incomplete activation of catalysts under these conditions. Contrarily, a high Al/Cr ratio promotes the catalytic activities in 1-6 complexes at a relatively high temperature (Table 2, entries 6, 12, 17, 24, 29, and 34) [7b, 13a, 18]. The precatalysts 1–2 and 4 were also investigated for ethylene oligomerization in the presence of MAO and toluene solvent, however, no improved results were obtained for tetramerization (Table 2, entries 3-4, 9-10 and 21-22). The precatalyst 2 having bulky cyclohexyl moiety upon Si produces 82% C₆ selectivity when activated with MAO in the presence of a toluene solvent (Table 2, entry 10). Moreover, activation of the precatalysts (1-2 and 4) using MAO in toluene solvent may also promote the formation of C₄ fraction (Table 2, entries 4, 10, and 22).

Under high ethylene pressure, all the precatalysts 1-6 showed improved C₈ selectivities at the expense of C₆ fractions (Table 3), and the highest selectivities of 71–72% within the liquid oligomeric fraction have been obtained respectively from precatalysts 1 and 4 under experimental conditions (Table 3, entries 8, 26 and 28). The precatalysts **1–6** show overall improved catalytic activities at high ethylene pressure and the highest activity of more than 25,300 g(product)·g(Cr)⁻¹·h⁻¹ with reasonable C₈ selectivity (63%) could be obtained by precatalyst **1** under experimental conditions (Table 3, entry 2). Along with the improved catalytic activity, the formation of branched co-oligomers (C₁₀-C₁₄) and higher oligomers (C₁₆₊) have also been observed and become more pronounced at the elevated temperature, suggesting the proportionality of the formation of these side-products with the productivity of the reaction (Table 3, entries 2–3, 6–7, 24, 18 and 35) [32]. Like the catalytic system reported by Zhang et al, the methylcyclopentane, and methylenecyclopentane fractions were found in all the oligomerization products in an almost 1:2 ratio and could be explained by the proposed mechanism [16].

To rationalize the C_8 selectivity and to explore the mechanistic aspects of Cr(III) complexes based on tridentate silicon bridged tris (diphenylphosphine) ligands, the catalyst **4** (best system in term of selectivity) was selected for DFT calculations [33]. The complex **4** was treated as a cationic Cr(I) specie which could be formed by the implication of cocatalyst and also is a prerequisite for ethylene

Table 3 Evaluation of 1–6 complexes for ethylene oligomerization at high ethylene pressure.^a

			Product selectivity (wt %)						
Entry	Precatalyst	Activity ^b	C4 ^c	C ₆ ^c	1-C ₆	C ₈ ^{c,l}	C ₁₀ -C ₁₄ ^c	C ₁₆₊ ^c	PE (g)
1	1	948	3	29	55	58	0	0	0.26
$2^{\mathbf{d},j}$		25,385	tr	21	62	63	2	9	0.28
3 ^e		10,500	tr	20	55	67	3	3	0.17
4 ^{e,f}		1515	3	35	63	61	0	0	0.87
5 ^f		2788	1	27	48	68	0	0	1.10
6^{g}		6981	2	17	76	28	14	30	0.35
7 ^h		13,981	3	25	76	20	16	17	0.43
8 ⁱ		3173	1	24	58	71	0	0	0.28
9 ^k		348	0	66	>99	33	0	0	0.12
10	2	1673	2	27	85	56	0	0	0.13
11 ^d		5538	1	35	60	63	0	0	0.08
$12^{d,j}$		9615	1	33	61	65	0	0	0.11
13 ^e		3211	1	31	61	67	0	0	0.10
14 ^{e,f}		425	7	56	48	36	0	0	0.09
15 ^f		1098	2	39	49	58	0	0	0.34
16 ^g		1752	3	48	73	48	0	0	0.10
17 ^h		1152	5	36	58	56	0	0	0.13
18 ⁱ		777	3	42	62	54	0	0	0.15
19 ^k		519	1	43	95	55	0	0	0.06
20 ^{d,g}	3	4173	3	38	87	53	0	0	0.17
21 ^{d,j}		2788	4	35	74	51	0	0	0.31
22 ^{e,f}		269	10	56	79	32	0	0	0.42
23 ^{e,i}		660	4	29	>99	51	0	0	0.26
24	4	2288	2	22	64	52	4	13	0.36
25 ^d		6250	1	29	65	66	0	0	0.29
26 ^e		5923	1	24	62	72	0	0	0.41
27 ^{e,f}		919	2	25	60	66	0	0	0.69
28 ⁱ		4558	tr	20	60	72	0	4	0.55
29 ^d	5	2385	4	43	58	52	0	0	0.37
30 ^{d,g}		4173	3	42	76	49	0	0	0.27
31 ^{d,j}		2885	4	33	61	56	0	0	0.41
32 ^{e,f}		415	4	32	72	52	0	0	0.94
33 ^d	6	1492	13	40	65	46	0	0	0.09
34 ^{d,g}		3769	5	45	67	48	0	0	0.18
35 ^{d,j}		4827	3	30	57	34	9	16	0.32
36 ^{e,f}		429	10	50	50	39	0	0	0.35

a General conditions: n(precatalyst), 4.8 μmol; pressure, 4.0 MPa; solvent, methylcyclohexane (20 mL); reaction time, 30 min; T, 45 °C; n(Al)/n(Cr), 500 equiv; n(DMAO)/n (AlEt₃), 4:1.

^b g(product) $g(Cr)^{-1} h^{-1}$.

^c wt % of liquid products (oligomers).

^d n(precatalyst), 1.2 μmol.

e n(precatalyst), 2.4 μmol.

^f T, 15 °C.

^g T, 60 °C.

^h *T*, 80 °C.

ⁱ *n*(Al)/*n*(Cr), 250 equiv.

^j *n*(Al)/*n*(Cr), 1000 equiv.

^k MAO.

¹ C_8 contains 100% 1- C_8 . tr = traces.

oligomerization, while the ligand was considered neutral after activation [27b].

Fig. 3 represents the relative free energy profiles for the selective formation of 1-hexene and 1-octene catalyzed by catalyst system 4. Initially, the subsequent spin crossing and oxidative coupling of two ethylene may convert the sextet bisethylene complex ⁶2 to guartet chromacyclopentane intermediate **3b**, which then provides three paths namely path 1 (single coordination pathway for C₈ formation), **path 2** (double coordination pathway for C_8 formation) and **path 3** (C_6 formation pathway) for further reaction. Following path 1, the coordination and subsequent insertion of third ethylene transformed the **3b** into chromacycloheptane intermediate **5** (rate-determining intermediate for **path 1** and **path** 3) via **TS_{4.5}** transition state. The intermediate **5** can have two choices at this instant, either coordinated with fourth ethylene molecule (needs 13.5 kcal/mol energy) to form 6a', or may follow path 3 and undergoes β -hydride elimination via TS_{5.9} (ratedetermining transition state in **path 3**) with an energy barrier of 23.0 kcal/mol energy and release 1-hexene. With the facilitation of low energy barrier, the intermediate 5 may prefer to coordinate with fourth ethylene molecule to form 6a' intermediate which stabilized itself to 6e and then transformed to intermediate 7 by passing through TS_{6e,7} (rate-determining transition state in path 1) with a barrier of 11.0 kcal/mol energy. The intermediate 7 then undergoes β -hydride elimination via **TS_{7.8}** with an energy barrier of 19.5 kcal/mol energy and release 1-octene. Taking path 2 into consideration, the double ethylene coordination (needs 17.6 kcal/mole energy) transformed 3b into intermediate 5' which then passes through TS_{5'.6a} (rate-determining transition state in path 2) with an energy barrier of 7.0 kcal/mol to form 6a. The intermediate **6a** stabilized itself to **6e**, passes through **TS**_{6e,7} to form **7**, and then release 1-C₈ via β -hydride elimination. It is worth mentioning that on **path 2** during double ethylene coordination, one of the diphenylphosphine moieties may temporarily lose its coordination with chromium center and the complex may behave as a bidentate catalyst at this instant (5', TS5',6a and 6a), however, quickly

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regained its tridenticity after one ethylene insertion (**6a**'). This phenomenon explains that one of the diphenylphosphine moieties of the complex has weak coordination with chromium center and may act as a hemilabile donor. This hemilabile phosphorus atom may provide a vacant site to the catalyst to simultaneously accommodate two ethylene molecules with chromacyclopentane intermediate and to allow double ethylene coordination. The results suggested that the presence of a hemilabile phosphorus atom is one of the main factors for the catalyst to produce high C₈ selectivity and only in this way the catalyst may follow the double ethylene coordination pathway.

The low energy barriers of ethylene coordination with the ratedetermining intermediates (**5** for **path 1** and **3b** for **path 2**) suggested that both single and double coordination may occur simultaneously and could produce C_8 fraction [34], nevertheless, the low energy transition state of **path 1** (18.6 kcal/mole energy) against **path 3** (23.0 kcal/mol energy) also suggested that **path 1** is the thermodynamically optimal pathway for C_8 formation. However, the role of high ethylene pressure could not be ignored on the double ethylene coordination pathway (**path 2**), as it is second order in ethylene and may be more favorable at high ethylene pressure [14,35]. Beyond the energy perspective, other factors like the role of experimental conditions, formation of active species for polymer production, and the formation of co-oligomerized fractions are equally important and can influence the C_8 selectivity and therefore should be taken into account [15].

4. Conclusions

In summary, we have reported the Cr(III) precatalysts based on tridentate silicon-bridged tris(diphenylphosphine) RSi(CH₂PPh₂)₃ and MeSi(CH₂)_n(PPh₂)₃-type ligands. Single crystal analysis, high-resolution mass-spectrometry, and elemental analysis revealed that these complexes may afford mononuclear tridentate coordination mode in which one diphenylphosphine moiety may act as a hemilabile donor. The DMAO/AlEt₃ activation transformed these complexes into active and selective tri/tetramerization catalyst systems. We found that steric bulk, electronic properties, the abstraction of methylene spacers, and experimental conditions effectively influence the activity and selectivity of these systems. Increasing the steric bulk or changing the electronic properties by substitution at silvl-moiety (in 2-3) or abstraction of methylene spacers (in **4**–**6**) may mediate the tri-/tetramerization switching. High ethylene pressure, low reaction temperature, and low Al/Cr ratio produce more C₈ fraction, while high temperature and high Al/Cr ratio offer improved catalytic activity. Precatalysts 1 and 4 proved efficient systems and offer 70% C8 selectivity in the liquid oligomeric fraction with considerable activity under suitable experimental conditions. Under 4.0 MPa ethylene pressure, the catalytic activity of more than 25,000 g(product) \cdot g(Cr)⁻¹ \cdot h⁻¹ was obtained by precatalyst 1 at 1.2 µmol catalyst loading, 45 °C temperature and 1000 equivalent of Al/Cr ratio. DFT calculations of catalyst **4** show that the single and double coordination pathways are simultaneously probable and can produce C₈ product, however, the single coordination pathway may provide an energetically facile route for C₈ formation.

Author contributions

The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Synthesis procedures, NMR characterizations, elemental analysis, HR-MS results, computational details, solvent corrected absolute free energies (Ha), electronic energies (Ha), and Cartesian coordinates (Å) of all the optimized structures and MECP, crystallographic data for **7** and CrCl₃(THF)-**L**² (PDF). Supplementary data to this article can be found online at https://doi.org/10.1016/j. jcat.2020.10.008.

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