

Article

# Preparation of Extremely Active Ethylene Tetramerization Catalyst $[iPrN(PAr_2)_2 - CrCl_2]^+ [B(C_6F_5)_4]^-$ (Ar = $-C_6H_4-p-SiR_3$ )

Jung Hyun Lee <sup>1,†</sup>, Jun Won Baek <sup>1,†</sup>, Dong Geun Lee <sup>1</sup>, Ji Hyeong Ko <sup>1</sup>, Dong Geun Lee <sup>2</sup>, Kye Sung Cho <sup>2</sup>, Jin Woo Lee <sup>2</sup> and Bun Yeoul Lee <sup>1,\*</sup>

<sup>1</sup> Department of Molecular Science and Technology, Ajou University, 206 Worldcup-ro, Yeongtong-gu, Suwon 16499, Korea; leejh23559@ajou.ac.kr (J.H.L.); btw91@ajou.ac.kr (J.W.B.); dg94.lee@hanwha-total.com (D.G.L.); jihyko7@naver.com (J.H.K.)

<sup>2</sup> Department of Base Chemical, Hanwha Total, 103, Dokgot 2-ro, Daesan-eup, Seosan-si 31900, Korea; axis.lee@hanwha-total.com (D.G.L.); kyesung@hanwha-total.com (K.S.C.); jinwoo13.lee@hanwha-total.com (J.W.L.)

\* Correspondence: bunyeoul@ajou.ac.kr; Tel.: +82-31-219-1844

† These authors contributed equally to this work.

**Abstract:** Numerous efforts have been made to achieve “on-purpose” 1-octene production since Sasol discovered a Cr-based selective ethylene tetramerization catalyst in the early 2000s. By preparing a series of bis(phosphine) ligands  $iPrN(PAr_2)_2$  where the Ar contains a bulky  $-SiR_3$  substituent (Ar =  $-C_6H_4-p-Si(nBu)_3$  (1),  $-C_6H_4-p-Si(1-hexyl)_3$  (2),  $-C_6H_4-p-Si(1-octyl)_3$  (3),  $-C_6H_4-p-Si(2-ethylhexyl)_3$  (4),  $-C_6H_4-p-Si(3,7-dimethyloctyl)_3$  (5)), we obtained an extremely active catalyst that meets the criteria for commercial utilization. The Cr complexes  $[iPrN(PAr_2)_2 - CrCl_2]^+ [B(C_6F_5)_4]^-$ , obtained by reacting ligands 1–5 with  $[(CH_3CN)_4CrCl_2]^+ [B(C_6F_5)_4]^-$ , showed high activity exceeding 6000 kg/g-Cr/h, when combined with the inexpensive  $iBu_3Al$ , thus avoiding the use of expensive modified methylaluminoxane (MMAO). The bulky  $-SiR_3$  substituents played a key role in the success of catalysis by blocking the formation of inactive species (Cr complexes coordinated by two  $iPrN(PAr_2)_2$  ligands, that is,  $[iPrN(PAr_2)_2 - CrCl_2]^+ [B(C_6F_5)_4]^-$ ). Among the complexes prepared,  $[3 - CrCl_2]^+ [B(C_6F_5)_4]^-$  exhibited the highest activity (11,100 kg/g-Cr/h, 100 kg/g-catalyst) with high 1-octene selectivity (75 wt%) and, moreover, mitigated the generation of undesired > C10 fractions (10.7 wt%). A 10-g-scale synthesis of 3 was developed, as well as a facile and low-cost synthetic method for  $[(CH_3CN)_4CrCl_2]^+ [B(C_6F_5)_4]^-$ .

**Keywords:** ethylene tetramerization; 1-octene production; chromium catalyst; bis(phosphine) ligand; tetrakis(pentafluorophenyl)borate



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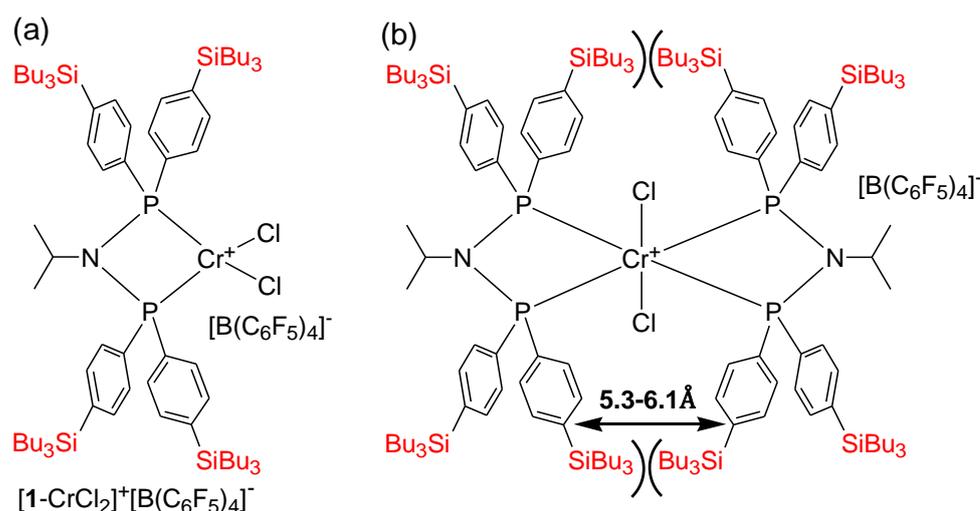
## 1. Introduction

Currently, 1-Octene is produced on a large scale (~1 million ton/y), consumed mainly as a comonomer in the ethylene polymerization processes, and its demand is increasing with the increase in the production of polyolefins with high 1-octene content, e.g., polyolefin elastomer (POE) in which the 1-octene content is substantial (~40 wt%). There are several manufacturing routes for 1-octene. It can be obtained in the Fischer-Tropsch process through either direct fractionation or chemical conversion of the heptene fraction [1]. In 2007, the Dow Chemical Company commercialized a route from butadiene, consisting of Pd-catalyzed telomerization of butadiene with methanol to yield 1-methoxy-2,7-octadiene, which is subsequently transformed to 1-octene [2,3]. The main route to 1-octene is the oligomerization of ethylene, using a nickel- or zirconium-based catalyst, in which a wide range of linear  $\alpha$ -olefins are generated, with the 1-octene fraction being less than 10% [4–6].

Catalysts that can selectively convert ethylene to 1-octene were discovered by Sasol in the early 2000s [7–9], while catalyst system that can selectively generate 1-hexene had been discovered ~10 years earlier, and were commercialized in the early 2000s [10–12].

Since the discovery of the ethylene tetramerization catalysts, numerous efforts have been made to develop so-called “on-purpose 1-octene production technology”, especially by companies that use 1-octene in large quantity (e.g., POE producers) [13–15]. The original Sasol catalyst system is composed of  $\text{Cr}(\text{acac})_3$ , a bis(phosphine) PNP-type ligand (e.g.,  $\text{iPrN}(\text{PPh}_2)_2$ ) and the substance known as modified methylaluminoxane (MMAO), and there have been several issues raised in the commercialization process. A serious issue is the use of the expensive MMAO in large excess ( $\text{Al}/\text{Cr}$ , ~500), which is a burden in terms of catalyst cost. Many attempts have been made to replace MMAO with stoichiometric amounts of  $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  or  $[\text{PhN}(\text{H})\text{Me}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ , but most of these attempts were unsuccessful [16–23], although the replacement of MMAO with non-coordinating anion based salts has been successful in olefin polymerization catalysis [24]. Sasol later disclosed, in a patent, a catalyst system that worked fairly efficiently without the use of MMAO [25]. Another critical issue is the generation of insoluble polyethylene (PE) as a side product. Even though the amount is typically small (<1%), the generated PE hampers the operation of a large scale continuous commercial process, causing a so called ‘fouling problem’. There is also a selectivity issue. Some 1-hexene is concomitantly generated, which is, however, a useful coproduct. Some useless compounds, such as methyl- and methylene-cyclopentane (cy-C6), and cotrimers containing two molecules of ethylene and one of 1-hexene or 1-octene (>C10), are also generated. The amount of the cy-C6 fraction is small (2–3%), but the amount of the cotrimers is substantial (10–15%).

Over the last 10 years, we have attempted to develop an efficient ethylene tetramerization catalyst, especially avoiding the use of expensive MMAO. Eventually, a cationic complex was synthesized in which chromium is coordinated by  $\text{iPrN}(\text{PAr}_2)_2$  ( $\text{Ar} = -\text{C}_6\text{H}_4-p\text{-Si}(\text{nBu})_3$ ) (**1**), paired with  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  (i.e.,  $[\text{1-CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ , Scheme 1a), and this gratifyingly showed extremely high activity (up to 6900 kg/g-Cr/h) when combined with inexpensive  $\text{iBu}_3\text{Al}$  [26–28]. With the aim of improving the activity further and with the hope of solving the concerns raised, we have synthesized derivatives of this highly active Cr complex, and the successful results of this are presented here. The development of catalysts for selective olefin oligomerization is a hot research topic in both academia and industry [29–39].



**Scheme 1.** A highly active ethylene tetramerization catalyst (a) and a hypothetical inactive  $[(\text{PNP})_2\text{CrCl}_2]^+$  species (b) constructed using  $\text{iPrN}(\text{PAr}_2)_2$  (**1**) ( $\text{Ar} = -\text{C}_6\text{H}_4-p\text{-Si}(\text{nBu})_3$ ).

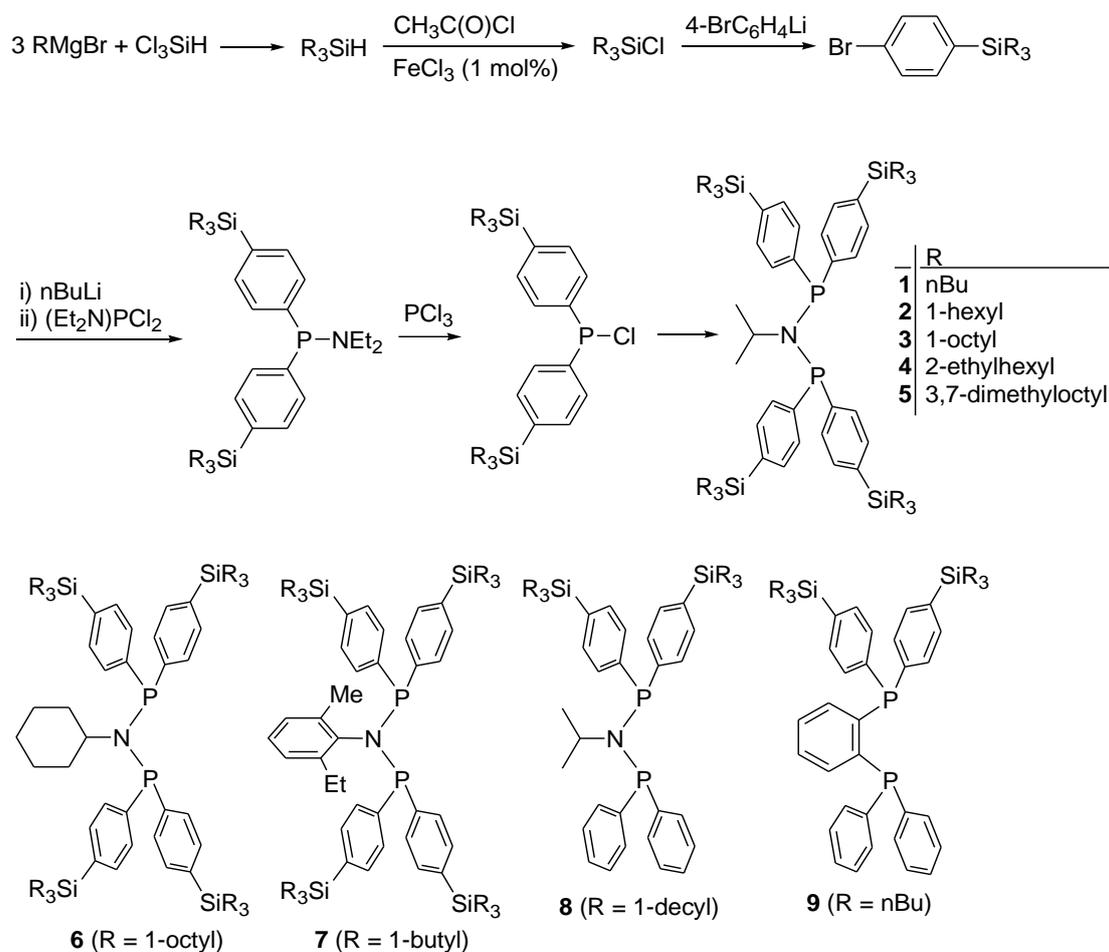
## 2. Results and Discussion

### 2.1. Preparation of Ligands

Once the chlorides in  $[(\text{PNP})\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  are replaced with alkyl by the action of trialkylaluminum, the commonly adopted ethylene tetramerization catalytic cycle involving cationic  $\text{Cr}^{\text{I/III}}$  species can operate [40–42]. On this basis, the preparation of  $[(\text{PNP})\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ -type complexes has previously been attempted, but attempts with the common bis (phosphine) PNP-type ligand  $i\text{PrN}(\text{PPh}_2)_2$  were unsuccessful. Instead of the intended species, cationic Cr complexes coordinated by two PNP ligands (i.e.,  $[(\text{PNP})_2\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ), which were reported to be inactive, were generated [20,26]. Gratifyingly, the desired  $[(\text{PNP})\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  type complex was obtained when the specially designed  $i\text{PrN}(\text{PAR}_2)_2$  ( $\text{Ar} = -\text{C}_6\text{H}_4\text{-}p\text{-Si}(\text{nBu})_3$ ) (**1**) was employed instead of the common  $i\text{PrN}(\text{PPh}_2)_2$  [28]. The tributylsilyl substituent ( $-\text{Si}(\text{nBu})_3$ ) plays a crucial role in this success; it hampers generation of the inactive  $[(\text{PNP})_2\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  type species because of steric repulsion between the two substituents (Scheme 1b), while negligibly influencing the electronic properties of the phosphine ligand (Hammett substituent constant  $\sigma$ , approximately  $-0.07$ ). Moreover, the bulky  $-\text{Si}(\text{nBu})_3$  substituents make the complex robust by hindering fluxional rotation around the N–P bond; the bonding between Cr and phosphine ligands is typically weak, and fluxional N–P bond rotation possibly triggers demetallation.

In previous work, we had prepared a series of  $i\text{PrN}(\text{PAR}_2)_2$  ligands ( $\text{Ar} = -\text{C}_6\text{H}_4\text{-}p\text{-SiMe}_3$ ,  $-\text{C}_6\text{H}_4\text{-}p\text{-SiEt}_3$ ,  $-\text{C}_6\text{H}_4\text{-}p\text{-Si}(\text{iPr})_3$ ,  $-\text{C}_6\text{H}_4\text{-}p\text{-Si}(\text{iPr})\text{Et}_2$ ,  $-\text{C}_6\text{H}_4\text{-}p\text{-Si}(\text{iPr})\text{Me}_2$ ,  $-\text{C}_6\text{H}_4\text{-}p\text{-Si}(\text{1-octyl})\text{Me}_2$ ) using commercially available  $\text{ClSiR}_3$  [28]. In the present work, we have prepared more derivatives, especially those containing the bulkier substituents  $-\text{Si}(\text{1-hexyl})_3$  (**2**),  $-\text{Si}(\text{1-octyl})_3$  (**3**),  $-\text{Si}(\text{2-ethylhexyl})_3$  (**4**) and  $-\text{Si}(\text{3,7-dimethyloctyl})_3$  (**5**), with an expectation that the bulkier group could more effectively prevent generation of the inactive  $[(\text{PNP})_2\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  species (Scheme 2). We expected that the formation of the ethylene/ethylene/1-octene and ethylene/ethylene/1-hexene cotrimers might be hindered by the bulky groups exerting steric repulsion against incoming 1-octene or 1-hexene substrates. One starting material,  $(\text{1-hexyl})_3\text{SiCl}$ , was commercially available, but the others, such as  $(\text{1-octyl})_3\text{SiCl}$ ,  $(\text{1-decyl})_3\text{SiCl}$ ,  $(\text{2-ethylhexyl})_3\text{SiCl}$  and  $(\text{3,7-dimethyloctyl})_3\text{SiCl}$  were not. These were prepared using the corresponding  $\text{R}_3\text{SiH}$  by employing the reported synthetic method, treatment of  $\text{R}_3\text{SiH}$  with  $\text{CH}_3\text{C}(\text{O})\text{Cl}$  in the presence of  $\text{FeCl}_3$  as catalyst (1 mol%) [43]. The yields were nearly quantitative, and the products were used without further purification after removal of the  $\text{FeCl}_3$  catalyst by filtration with hexane. Only  $(\text{1-octyl})_3\text{SiH}$  was commercially available, while the other compounds ( $\text{R}_3\text{SiH}$ ,  $\text{R} = \text{1-decyl}$ ,  $\text{2-ethylhexyl}$  or  $\text{3,7-dimethyloctyl}$ ) were prepared by reacting  $\text{Cl}_3\text{SiH}$  with  $\text{RMgCl}$  or  $\text{RMgBr}$ .

Using the prepared  $\text{R}_3\text{SiCl}$  ( $\text{R} = \text{1-octyl}$ ,  $\text{2-ethylhexyl}$  or  $\text{3,7-dimethyloctyl}$ ) and the purchased  $(\text{1-hexyl})_3\text{SiCl}$ , the bis (phosphine) ligands  $i\text{PrN}(\text{PAR}_2)_2$  ( $\text{Ar} = -\text{C}_6\text{H}_4\text{-}p\text{-SiR}_3$ ) were prepared according to a previously developed synthetic route (Scheme 2) [28]. With the aim of commercialization, a rather large scale (10 g scale) synthesis of  $i\text{PrN}(\text{PAR}_2)_2$  ( $\text{Ar} = -\text{C}_6\text{H}_4\text{-}p\text{-Si}(\text{1-octyl})_3$ ) was attempted. 1,4-Dibromobenzene was treated with  $n\text{BuLi}$  in THF at  $-78^\circ\text{C}$  to generate 1-bromo-4-lithiobenzene, which was reacted with  $(\text{1-octyl})_3\text{SiCl}$  to obtain 1-bromo-4-( $\text{R}_3\text{Si}$ )-benzene ( $\text{R} = \text{1-octyl}$ ). A slight excess of dibromobenzene (1.1 eq per  $n\text{BuLi}$ ) was used in order to minimize formation of the bis(silylated) compound  $1,4\text{-(R}_3\text{Si)}_2\text{C}_6\text{H}_4$  ( $\text{R} = \text{1-octyl}$ ). The remaining unreacted 1,4-dibromobenzene could be removed simply by evacuation at  $70^\circ\text{C}$ , and any  $(\text{1-octyl})_3\text{SiCl}$  remaining unreacted was removed using a small amount of silica gel, where it was attached by forming a Si–O bond with the generation of HCl, enabling its removal via filtration. 1-Bromo-4-lithiobenzene should be used in situ as generated at a low temperature; an explosion occurred during an attempt to isolate it.



**Scheme 2.** Synthesis of bis (phosphine) ligands for ethylene tetramerization catalysts.

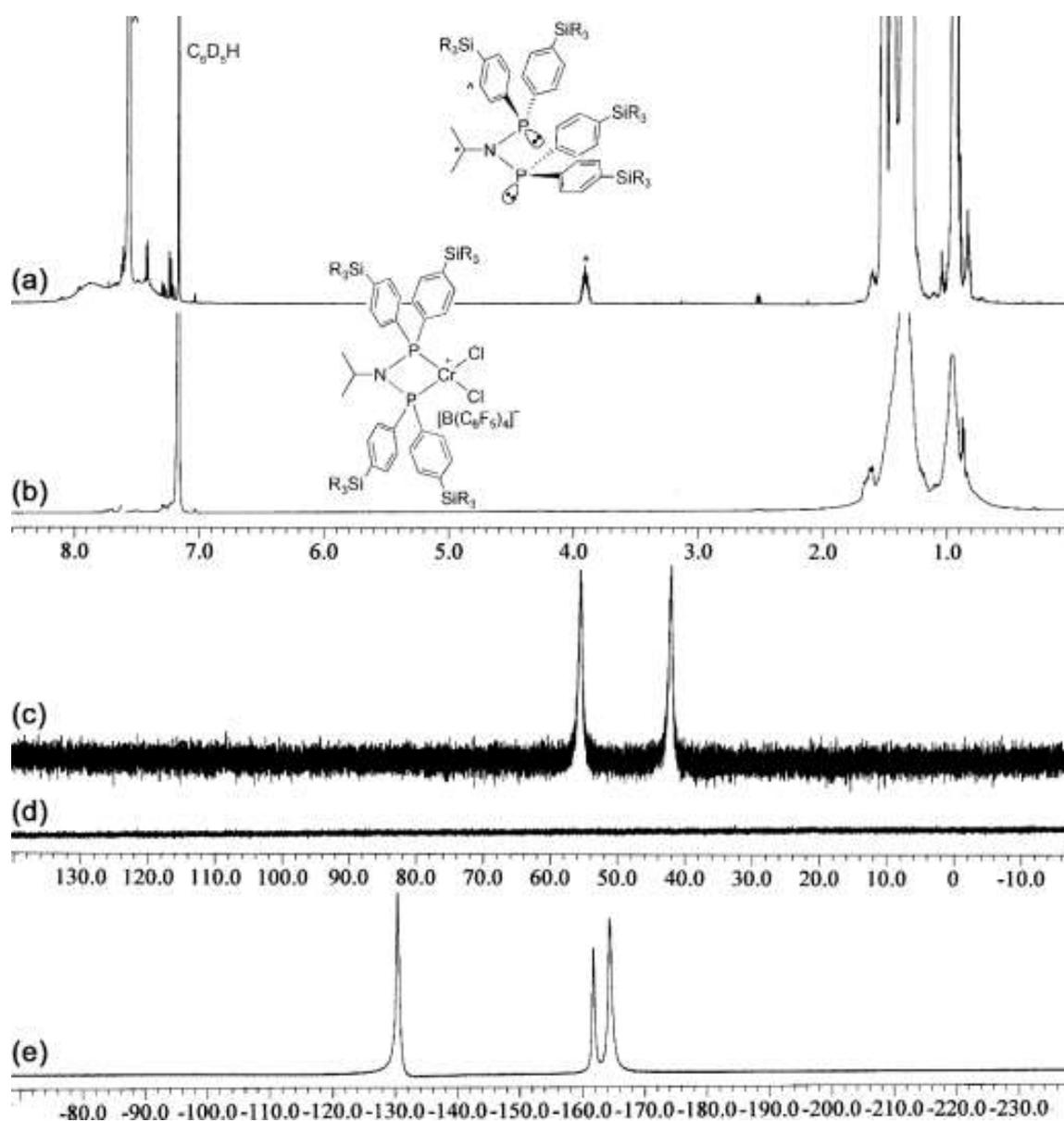
The second step, the conversion of 1-bromo-4-(R<sub>3</sub>Si)-benzene to Et<sub>2</sub>N-P(Ar)<sub>2</sub> (Ar = -C<sub>6</sub>H<sub>4</sub>-p-SiR<sub>3</sub>), was rather tricky. In the conversion of *p*-(R<sub>3</sub>Si)-C<sub>6</sub>H<sub>4</sub>-Br to *p*-(R<sub>3</sub>Si)-C<sub>6</sub>H<sub>4</sub>-Li with nBuLi, nBu-Br is inevitably formed as a byproduct, and this could react with the product Et<sub>2</sub>N-P(Ar)<sub>2</sub>, since nBu-Br is an electrophile and Et<sub>2</sub>N-P(Ar)<sub>2</sub> is a good nucleophile. In order to prevent such side reactions, the reaction temperature should be maintained at -78 °C, and the work-up procedure should be carefully controlled. However, it was found possible to avoid this awkward situation by performing the reaction of *p*-(R<sub>3</sub>Si)-C<sub>6</sub>H<sub>4</sub>-Li with Et<sub>2</sub>NPCl<sub>2</sub> after removal of byproduct nBu-Br. The boiling point of nBu-Br is 102 °C, and it could be removed by evacuation after the generation of *p*-(R<sub>3</sub>Si)-C<sub>6</sub>H<sub>4</sub>-Li in toluene/ether (*w/w* 3:1) at -30 °C. Some excess nBuLi (1.3 eq per *p*-(R<sub>3</sub>Si)-C<sub>6</sub>H<sub>4</sub>-Br) was added for complete conversion of *p*-(R<sub>3</sub>Si)-C<sub>6</sub>H<sub>4</sub>-Br to *p*-(R<sub>3</sub>Si)-C<sub>6</sub>H<sub>4</sub>-Li because when the stoichiometric amount of nBuLi was used, some portion of reactant *p*-(R<sub>3</sub>Si)-C<sub>6</sub>H<sub>4</sub>-Br (~5%) remained unconverted. The nBuLi that remained unreacted owing to the excess addition was destroyed during the course of the evacuation process; it reacted with nBu-Br at room temperature and was converted to inert nBu-H and LiBr. After dissolving the *p*-(R<sub>3</sub>Si)-C<sub>6</sub>H<sub>4</sub>-Li in cold THF (-30 °C), Et<sub>2</sub>NPCl<sub>2</sub> was added to obtain the desired Et<sub>2</sub>N-P(Ar)<sub>2</sub> (Ar = -C<sub>6</sub>H<sub>4</sub>-p-SiR<sub>3</sub>). A slightly excess of Et<sub>2</sub>NPCl<sub>2</sub> (0.52 eq per *p*-(R<sub>3</sub>Si)-C<sub>6</sub>H<sub>4</sub>-Br) was added for complete consumption of *p*-(R<sub>3</sub>Si)-C<sub>6</sub>H<sub>4</sub>-Li, and the side product Et<sub>2</sub>N-P(Cl)Ar (Ar = -C<sub>6</sub>H<sub>4</sub>-p-SiR<sub>3</sub>) formed in the presence of the slight excess of Et<sub>2</sub>NPCl<sub>2</sub> was removed using a small amount of silica gel. While the product Et<sub>2</sub>N-P(Ar)<sub>2</sub> (Ar = -C<sub>6</sub>H<sub>4</sub>-p-SiR<sub>3</sub>) was intact on the silica surface, Et<sub>2</sub>N-P(Cl)Ar was chemically attached to the silica surface by forming a ≡SiO-P(Ar)(NEt<sub>2</sub>) bond.

$\text{Et}_2\text{N-PAr}_2$  ( $\text{Ar} = -\text{C}_6\text{H}_4\text{-}p\text{-SiR}_3$ ) was cleanly converted to  $\text{Cl-PAr}_2$  when it was dissolved in neat  $\text{PCl}_3$  (5.5 eq) and then heated at  $70^\circ\text{C}$  for 2 h [44]. Unreacted  $\text{PCl}_3$  and byproduct  $\text{Et}_2\text{N-PCl}_2$  were removed by distillation under reduced pressure; the boiling points of  $\text{PCl}_3$  and  $\text{Et}_2\text{N-PCl}_2$  are  $76^\circ\text{C}$  and  $179^\circ\text{C}$ , respectively, and they were easily separated for reuse. The target ligand  $\text{iPrN(PAr}_2)_2$  ( $\text{Ar} = -\text{C}_6\text{H}_4\text{-}p\text{-SiR}_3$ ) was obtained by the routine method of reacting  $\text{Cl-PAr}_2$  with  $\text{iPrNH}_2$  in  $\text{CH}_2\text{Cl}_2$  in the presence of  $\text{Et}_3\text{N}$  (10 eq per  $\text{iPrNH}_2$ ). A slight excess of  $\text{Cl-PAr}_2$  (2.2 eq per  $\text{iPrNH}_2$ ) was used to ensure complete conversion of  $\text{iPrNH}_2$  to  $\text{iPrN(PAr}_2)_2$ , without leaving intermediate  $\text{iPrN(H)(PAr}_2)$ . The unreacted  $\text{Cl-PAr}_2$  remaining due to the excess addition could be removed by addition of a small amount of silica gel, to which  $\text{Cl-PAr}_2$  was attached by forming a  $\equiv\text{SiO-PAr}_2$  bond.

In the  $^1\text{H}$  NMR spectrum of  $\text{iPrN(PAr}_2)_2$  ( $\text{Ar} = -\text{C}_6\text{H}_4\text{-}p\text{-Si(1-octyl)}_3$ ) (Figure 1a), a signal corresponded to  $\text{N-CHMe}_2$  was distinctly observed at 3.90 ppm as a multiplet coupled with methyl protons and the two phosphorous atoms. Impurity signals were observed at 2.51 ppm as a triplet ( $J = 7.8$  Hz) and at 7.23 and 7.41 ppm as doublets overlapped with the product signals, which were assigned to  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{-C}_6\text{H}_4\text{-}p\text{-SiR}_3$  generated at the stage of conversion of  $\text{Br-C}_6\text{H}_4\text{-}p\text{-SiR}_3$  to  $\text{Li-C}_6\text{H}_4\text{-}p\text{-SiR}_3$ . There was no way to remove the impurities; the product was highly soluble in most organic solvents, thus not permitting its crystallization, and its molecular weight was too high to perform vacuum distillation (1894 Da). Even though the signal intensity at 2.51 ppm assigned to the impurity was substantial (8.8%) relative to the product signal at 3.90 ppm, the amount of impurity as a weight percentage was negligible (1.2 wt%). The signal corresponding to the ortho-protons on  $-\text{C}_6\text{H}_4\text{-}p\text{-SiR}_3$  moieties was typically very broad at 7.0–8.0 ppm while that corresponding to the meta-protons was sharp at 7.56 ppm as a doublet coupled with the ortho-protons ( $J = 6.6$  Hz). Two signals were distinctly observed at 55.5 ppm and 42.1 ppm in the  $^{31}\text{P}$  NMR spectrum (Figure 1c), which we attribute to restricted rotation around the P–N bonds; the two phosphorus atoms are inequivalent in the most stable resting state [27].

By replacing  $\text{iPrNH}_2$  with cyclohexylamine, an analogous ligand,  $\text{C}_6\text{H}_{11}\text{N(PAr}_2)_2$  ( $\text{Ar} = -\text{C}_6\text{H}_4\text{-}p\text{-Si(1-octyl)}_3$ ) (6), was also cleanly obtained, and the  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectrum features were the same as those of the ligand constructed using  $\text{iPrNH}_2$  (Figures S1 and S25). A PNP ligand constructed with 2-ethyl-6-methylaniline, 2-Et-6-Me- $\text{C}_6\text{H}_3\text{N(PAr}_2)_2$  ( $\text{Ar} = \text{C}_6\text{H}_4\text{-meta-Me}$ ), has been reported to exhibit good performance, and 2-Et-6-Me- $\text{C}_6\text{H}_3\text{N(PAr}_2)_2$  ( $\text{Ar} = -\text{C}_6\text{H}_4\text{-}p\text{-Si(nBu)}_3$ ) (7) was prepared by replacing  $\text{iPrNH}_2$  with 2-ethyl-6-methylaniline [45]. The  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra of 7 were different from those constructed with  $\text{iPrNH}_2$  and cyclohexylamine (Figures S1 and S26). A single signal was observed at 57.0 ppm in the  $^{31}\text{P}$  NMR spectrum of 7, whereas two signals were observed for the ligands constructed with  $\text{iPrNH}_2$  and cyclohexylamine. Both ortho- and meta-protons of  $-\text{C}_6\text{H}_4\text{-}p\text{-Si(nBu)}_3$  were observed as sharp signals at 7.82 (t), 7.79 (t), 7.49 (d) and 7.46 (d) ppm, clearly exhibiting a splitting pattern.

The desired  $\text{iPrN(PAr}_2)_2$  was not obtained from  $\text{Cl-PAr}_2$  ( $\text{Ar} = -\text{C}_6\text{H}_4\text{-}p\text{-Si(1-decyl)}_3$ ), which contained the bulkiest 1-decyl substituents; in many attempts, the reaction stopped at the intermediate stage of  $\text{iPrN(H)(PAr}_2)$ . Instead of  $\text{iPrN(PAr}_2)_2$ , the unsymmetrical  $\text{iPrN(PAr}_2)(\text{PPh}_2)$  ( $\text{Ar} = -\text{C}_6\text{H}_4\text{-}p\text{-Si(1-decyl)}_3$ ) (8) was prepared by reacting  $\text{iPrN(H)(PAr}_2)$  with  $\text{Cl-PPh}_2$ . A chromium complex constructed with an ortho-phenylene-bridged bis(phosphine) ligand,  $[\text{ortho-C}_6\text{H}_4(\text{PPh}_2)_2]\text{CrCl}_3$ , was reported to show as high activity as that constructed with  $\text{iPrN(PPh}_2)_2$  [46]. The synthesis of  $\text{ortho-C}_6\text{H}_4(\text{PAr}_2)_2$  ( $\text{Ar} = -\text{C}_6\text{H}_4\text{-}p\text{-Si(nBu)}_3$ ) was therefore attempted according to the method developed for  $\text{ortho-C}_6\text{H}_4(\text{PPh}_2)_2$ , reaction of  $\text{KP}[\text{C}_6\text{H}_4\text{-}p\text{-Si(nBu)}_3]_2$  (prepared from  $\text{Cl-P}[\text{C}_6\text{H}_4\text{-}p\text{-Si(nBu)}_3]_2$  and potassium metal) with  $\text{ortho-C}_6\text{H}_4\text{F}_2$ , but the desired compound was not cleanly afforded [47]. However, an unsymmetrical ligand  $\text{ortho-C}_6\text{H}_4(\text{PAr}_2)(\text{PPh}_2)$  ( $\text{Ar} = -\text{C}_6\text{H}_4\text{-}p\text{-Si(nBu)}_3$ ) (9) was successfully prepared by reacting  $\text{ortho-C}_6\text{H}_4(\text{PPh}_2)\text{Li}$  with  $\text{Cl-PAr}_2$  (Scheme 2). In the  $^{31}\text{P}$  NMR spectrum of the product, two phosphorus signals were observed as sharp doublet ( $J = 157$  Hz) signals at  $-12.0$  and  $-12.9$  ppm.

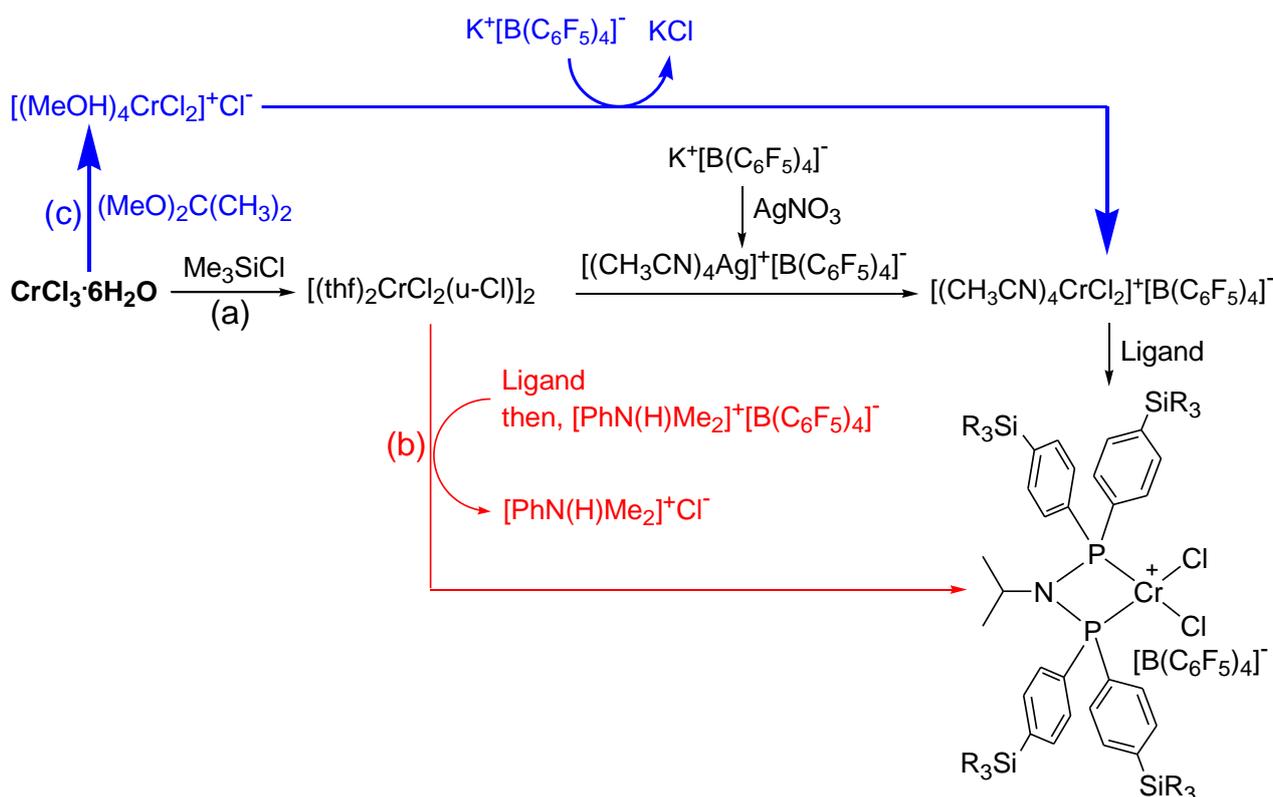


**Figure 1.**  $^1\text{H}$  NMR spectra of **3** and  $[\mathbf{3}-\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  (a,b),  $^{31}\text{P}$  NMR spectra of **3** and  $[\mathbf{3}-\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  (c,d) and  $^{19}\text{F}$  NMR spectrum of  $[\mathbf{3}-\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  (e).

## 2.2. Preparation of Chromium Complexes

Ligands **1–9** were reacted with  $[(\text{CH}_3\text{CN})_4\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  in  $\text{CH}_2\text{Cl}_2$  with the aim of obtaining complexes of the type  $[(\text{PNP})-\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  (Scheme 3a). These ligands are highly soluble in methylcyclohexene, the solvent in which the ethylene tetramerization reaction is typically performed, whereas  $[(\text{CH}_3\text{CN})_4\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  is completely insoluble in this solvent. The resultants in the reaction pots of **1–8** and  $[(\text{CH}_3\text{CN})_4\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  were soluble in methylcyclohexene, leaving a negligible amount of insoluble fraction, indicating that the  $[(\text{PNP})-\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ -type complexes were successfully formed. On coordination of these ligands to the paramagnetic Cr(III) center, aromatic signals assigned to the  $-\text{C}_6\text{H}_4-p\text{-SiR}_3$  moiety were not detected in the  $^1\text{H}$  NMR spectra (Figure 1b), and  $^{31}\text{P}$  NMR signals were also not detected (Figure 1d). Three signals assigned to ortho-, meta- and para-F on the outer-sphere  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  were observed in the  $^{19}\text{F}$  NMR spectra (Figure 1e). Typically, Cr(III) complexes persist in adopting an octahedral coordination mode, and we surmise that  $[(\text{PNP})-\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  may exist either in a form coordinated additionally by  $\text{CH}_3\text{CN}$  (i.e.,  $[(\text{PNP})-\text{CrCl}_2(\text{NCCH}_3)_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ) or in a

dinuclear form (i.e.,  $[(PNP)-CrCl(\mu-Cl)(NCCH_3)]_2^+[B(C_6F_5)_4]_2^-$ ). The structure of the latter has previously been elucidated by X-ray crystallography [28]. Thorough removal of any residual  $CH_3CN$  (along with any residual  $CH_2Cl_2$ ) was needed to maximize the activity. The complexes were stable for several months as solutions in methylcyclohexane (0.1–10 wt%), provided contamination with water or polar compounds was scrupulously avoided. The reaction product of *ortho*- $C_6H_4(PAr_2)(PPh_2)$  ( $Ar = -C_6H_4-p-Si(nBu)_3$ ) (9) with  $[(CH_3CN)_4CrCl_2]^+[B(C_6F_5)_4]^-$  was insoluble in methylcyclohexane.



**Scheme 3.** Synthetic routes for  $[iPrN(PAr_2)_2CrCl_2]^+[B(C_6F_5)_4]^-$  ( $Ar = -C_6H_4-p-SiR_3$ ) (a, original route; b and c, simplified routes in this work).

Even though the cationic Cr precursor ( $[(CH_3CN)_4CrCl_2]^+[B(C_6F_5)_4]^-$ ) can be prepared in a pure, crystalline form using a well-defined Cr source  $[CrCl_2(\mu-Cl)(thf)_2]_2$  [48], its large-scale preparation is still a burden, requiring expensive  $AgNO_3$  and tedious recrystallization processes with moderate yields (70–80% and 60–80% for each step);  $K^+[B(C_6F_5)_4]^-$  is first converted to  $[(CH_3CN)_4Ag]^+[B(C_6F_5)_4]^-$  using expensive  $AgNO_3$ , and  $[(CH_3CN)_4Ag]^+[B(C_6F_5)_4]^-$  is then converted to  $[(CH_3CN)_4CrCl_2]^+[B(C_6F_5)_4]^-$  by reaction with  $[CrCl_2(\mu-Cl)(thf)_2]_2$  (Scheme 3a). The large-scale preparation of  $[CrCl_2(\mu-Cl)(thf)_2]_2$  also requires a recrystallization process to obtain a pure compound in moderate yield (70%). Hence, another convenient route was chosen in an attempt to prepare  $[iPrN(PAr_2)_2-CrCl_2]^+[B(C_6F_5)_4]^-$  ( $Ar = -C_6H_4-p-Si(1-octyl)_3$ ) (Scheme 3b) [28]. Addition of  $iPrN(PAr_2)_2$  to a slurry of  $[CrCl_2(\mu-Cl)(thf)_2]_2$  in  $CH_2Cl_2$  resulted in the immediate formation of a blue solution. When  $[PhN(H)Me_2]^+[B(C_6F_5)_4]^-$ , which is currently used on a large scale in the polyolefin industry, was added to the resulting blue solution, the color of the solution immediately changed to green. After completely removing the volatiles using a vacuum line, the residue was treated with methylcyclohexane. Most of the residue dissolved to afford a bluish-green solution with a small amount of insoluble  $[PhN(H)Me_2]Cl$ , which was removed by filtration. However, the solution was slightly different in color from that prepared with  $[(CH_3CN)_4CrCl_2]^+[B(C_6F_5)_4]^-$  (blue-green vs. green), implying that the resultant was not genuine  $[iPrN(PAr_2)_2-CrCl_2]^+[B(C_6F_5)_4]^-$  but was contaminated

with blue neutral complex  $iPrN(PAr_2)_2-CrCl_3$ . The Cr complex obtained by this simple method exhibited fairly high activity (5200 kg/g-Cr/h), but only half as great as that of the complex prepared with  $[(CH_3CN)_4CrCl_2]^+[B(C_6F_5)_4]^-$  (11,100 kg/g-Cr/h).

Finally, we developed a facile and low-cost method for the synthesis of  $[(CH_3CN)_4CrCl_2]^+[B(C_6F_5)_4]^-$  (Scheme 3c). The structure of the most common and inexpensive Cr source,  $CrCl_3 \cdot 6H_2O$ , is known to be  $[(H_2O)_4CrCl_2]^+Cl^- \cdot 2(H_2O)$  from which  $[(CH_3OH)_4CrCl_2]^+Cl^-$  could be easily obtained in good yield (>90%). When  $[(H_2O)_4CrCl_2]^+Cl^- \cdot 2(H_2O)$  was treated with 2,2-dimethoxypropane  $((CH_3)_2C(OMe)_2$ , acetone dimethyl ketal), the water molecules in  $[(H_2O)_4CrCl_2]^+Cl^- \cdot 2(H_2O)$  were converted into methanol and acetone molecules, eventually affording  $[(CH_3OH)_4CrCl_2]^+Cl^-$  [49]. The isolated green solid  $[(CH_3OH)_4CrCl_2]^+Cl^-$  was dissolved in ethanol and treated with  $K^+[B(C_6F_5)_4]^-$  to yield  $[(ROH)_4CrCl_2]^+[B(C_6F_5)_4]^-$  (R = Me or Et) with precipitation of KCl (solubility of KCl in ethanol, 2.88 mg/L at 25 °C). The ROH in  $[(ROH)_4CrCl_2]^+[B(C_6F_5)_4]^-$  could be replaced with  $CH_3CN$  by repeated dissolution in  $CH_3CN$  and evaporation under vacuum, finally affording the desired complex  $[(CH_3CN)_4CrCl_2]^+[B(C_6F_5)_4]^-$  in good yield (88%).

### 2.3. Oligomerization Studies

The prepared chromium complexes were investigated for ethylene tetramerization in a 500 mL scale reactor at a controlled reaction temperature (40 °C or 60 °C) and ethylene pressure (35 bar). The chromium complex of ligand **2** containing  $-Si(1-hexyl)_3$  substituents,  $[2-CrCl_2]^+[B(C_6F_5)_4]^-$ , exhibited an activity comparable to that of  $[1-CrCl_2]^+[B(C_6F_5)_4]^-$  containing  $-Si(nBu)_3$  substituents (6400 kg/g-Cr/h vs. 6900 kg/g-Cr/h; entries 1 and 2 in Table 1). Gratifyingly,  $[3-CrCl_2]^+[B(C_6F_5)_4]^-$  containing  $-Si(1-octyl)_3$  substituents showed a 1.6-times enhanced activity (11,100 kg/g-Cr/h; entry 3 in Table 1). On increasing the reaction temperature from 40 °C to 60 °C, the activity was further enhanced to 12,500 kg/g-Cr/h (entry 4). Such extremely high activity values, exceeding 10,000 kg/g-Cr/h, have rarely been reported [13]. In a patent granted to Dow Chemical Company, an extremely high activity of up to 14,000 kg/g-Cr/h was recorded in a high-throughput screening apparatus under the conditions of 45 °C and 34 bar ethylene pressure with a catalyst system composed of  $nBuN[P(C_6H_4-o-F)_2][P(2,5-Ph_2C_4H_6)]$ ,  $CrCl_3(thf)_3$ , and MMAO (Al/Cr = 1000) [50]. In a patent granted to Sasol Technology, an extremely high activity of 12,400 kg/g-Cr/h was reported with a catalyst system composed of  $iPrN(PPh_2)(P(Ar)Ph)$  (Ar =  $C_6H_4-o-OCF_3$ ),  $Cr(acac)_3$  and MMAO (Al/Cr = 1000) [51]. When the  $-Si(1-octyl)_3$  substituents in  $[3-CrCl_2]^+[B(C_6F_5)_4]^-$  were replaced with the substituents having the same carbon number but with a branched structure, i.e.,  $-Si(2-ethylhexyl)_3$ , the activity was reduced back to the level of those bearing  $-Si(1-hexyl)_3$  or  $-Si(nBu)_3$  substituents (7000 kg/g-Cr/h; entry 5). Introducing greater steric bulkiness, either by replacing  $-Si(1-octyl)_3$  substituents with  $-Si(3,7-dimethyloctyl)_3$  or replacing the  $iPrN-$  moiety with a cyclohexylN- moiety, slightly reduced the activity from 11,000 to 9000 kg/g-Cr/h (entries 6 and 7).

**Table 1.** Results for ethylene tetramerization reactions <sup>a</sup>.

Entry	Catalyst (Substituent)	Activity (Kg/g-Cr/h)	1-C8 (wt%)	1-C6 (wt%)	cy-C6 (wt%) <sup>b</sup>	>C10 (wt%)	PE (wt%)
1	$[1-CrCl_2]^+[B(C_6F_5)_4]^-$ ( $-Si(nBu)_3$ )	6900	75.0	8.1	4.0	12.6	0.3
2	$[2-CrCl_2]^+[B(C_6F_5)_4]^-$ ( $-Si(1-hexyl)_3$ )	6400	75.2	8.2	4.4	12.0	0.2
3	$[3-CrCl_2]^+[B(C_6F_5)_4]^-$ ( $-Si(1-octyl)_3$ )	11,100	75.0	9.2	4.9	10.7	0.2
4 <sup>c</sup>	$[3-CrCl_2]^+[B(C_6F_5)_4]^-$ ( $-Si(1-octyl)_3$ )	12,500	56.1	25.2	4.2	13.6	1.0
5	$[4-CrCl_2]^+[B(C_6F_5)_4]^-$ ( $-Si(2-ethylhexyl)_3$ )	7000	64.7	11.4	8.9	14.7	0.2
6	$[5-CrCl_2]^+[B(C_6F_5)_4]^-$ ( $-Si(3,7-dimethyloctyl)_3$ )	8900	70.1	9.4	5.0	15.2	0.3
7	$[6-CrCl_2]^+[B(C_6F_5)_4]^-$ ( $C_6H_{11}N-$ ; $-Si(1-octyl)_3$ )	9200	74.0	9.1	4.7	12.0	0.1
8	$[8-CrCl_2]^+[B(C_6F_5)_4]^-$ (asymmetric)	7200	69.5	12.2	5.1	11.3	1.9

<sup>a</sup> Conditions: Cr-complex (2.8 μmol),  $iBu_3Al$  (750 μmol), methylcyclohexane (200 mL), ethylene (35 bar), 40 °C, 30 min. <sup>b</sup> Methylene-cyclopentane and methylcyclopentane. <sup>c</sup> Reaction temperature of 60 °C.

The Cr complex constructed with **7** (i.e., 2-Et-6-Me-C<sub>6</sub>H<sub>3</sub>N(PAr<sub>2</sub>)<sub>2</sub>, Ar = -C<sub>6</sub>H<sub>4</sub>-*p*-Si(nBu)<sub>3</sub>), which was prepared by replacing iPrNH<sub>2</sub> with 2-ethyl-6-methylaniline, generated many polymers filling the reactor fully. A single signal was observed in the <sup>31</sup>P NMR spectrum of ligand **7**, which is in contrast with the observation of two signals in the spectra of ligands **1–6** that afforded highly active catalysts. In the <sup>1</sup>H NMR spectra of **1–6**, the signal corresponding to the ortho-protons in the -C<sub>6</sub>H<sub>4</sub>-*p*-Si(nBu)<sub>3</sub> substituents was very broad, but the corresponding signals of **7** were sharp, and clearly showed a coupling pattern. Observation of the broad proton signal and the two phosphorus signals in the <sup>1</sup>H and <sup>31</sup>P NMR spectra of **1–6** was attributed to restricted rotation around the P–N bonds [27]. Rotation around the P–N bonds is not restricted in **7**, which showed sharp proton signals as well as a single phosphorus signal, and the rotation may trigger de-coordination of the PNP ligand from the Cr center. We assumed that polymers were generated once the PNP ligand was detached from the Cr center during the oligomerization process. The complex [8–CrCl<sub>2</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup> constructed with the unsymmetrical ligand iPrN(PAr<sub>2</sub>)(PPh<sub>2</sub>) (Ar = -C<sub>6</sub>H<sub>4</sub>-*p*-Si(1-decyl)<sub>3</sub>) was also highly active, but its activity was lower than that of [3–CrCl<sub>2</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup> (7200 vs. 11100 kg/g-Cr/h; entry 8). The reaction product of ligand **9** with [(CH<sub>3</sub>CN)<sub>4</sub>CrCl<sub>2</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup> was insoluble in methylcyclohexane, and was inactive under identical tetramerization conditions.

The complexes [1–CrCl<sub>2</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup>, [2–CrCl<sub>2</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup> and [3–CrCl<sub>2</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup> containing -Si(nBu)<sub>3</sub>, -Si(1-hexyl)<sub>3</sub> and -Si(1-octyl)<sub>3</sub> substituents, respectively, exhibited the same high level of selectivity for 1-octene (75.0–75.2 wt%). Complex [3–CrCl<sub>2</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup>, which showed the highest activity, advantageously generated slightly less of the useless >C10 fraction (mainly the ethylene/ethylene/1-octene and ethylene/ethylene/1-hexene cotrimers) but produced a slightly larger amount of 1-hexene than [1–CrCl<sub>2</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup> or [2–CrCl<sub>2</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup> (>C10: 10.7 wt% vs. 12.6–12.0 wt%; 1-hexene: 9.2 wt% vs. 8.1–8.2 wt%). The 1-octene selectivity of [3–CrCl<sub>2</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup> deteriorated from 75.0% to 56.1% on increasing the reaction temperature from 40 °C to 60 °C, and a larger amount of 1-hexene was generated at the higher temperature (9.2 wt% at 40 °C vs. 25.2 wt% at 60 °C; entry 3 vs. entry 4, Table 1). The 1-octene selectivity also deteriorated from 75.0 wt% to 64.7 or 70.1 wt% on replacing -Si(1-octyl)<sub>3</sub> substituents with -Si(2-ethylhexyl)<sub>3</sub> or -Si(3,7-dimethyloctyl)<sub>3</sub>; instead, a larger amount of the >C10 fraction was generated by this replacement (10.7 wt% vs. 14.7 and 15.2 wt%; entries 5 and 6, Table 1). It has been proposed that the amount of cy-C6 fraction (methylenecyclopentane and methylcyclopentane) is correlated with the amount of 1-hexene generated [33]. The lowest amount of 1-hexene (8.1 wt%) and also the lowest amount of the cy-C6 fraction (4.0 wt%; entry 1) was generated with [1–CrCl<sub>2</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup>; and the highest amount of 1-hexene (11.4 wt%) and also the highest amount of cy-C6 fraction (8.9 wt%) was generated with [4–CrCl<sub>2</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup> containing the -Si(2-ethylhexyl)<sub>3</sub> substituent. The complex [3–CrCl<sub>2</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup>, which showed the highest activity, generated 4.9 wt% of the cy-C6 fraction. A small amount of PE was generated in most cases (0.1–0.3 wt%). In the reaction batch performed with [3–CrCl<sub>2</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup> at the higher temperature of 60 °C, a larger amount of PE was generated (1.0 wt%; entry 4). The complex [8–CrCl<sub>2</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup> constructed with the unsymmetrical ligand iPrN(PAr<sub>2</sub>)(PPh<sub>2</sub>) (Ar = -C<sub>6</sub>H<sub>4</sub>-*p*-Si(1-decyl)<sub>3</sub>) generated a relatively larger amount of PE (1.9 wt%, entry 8).

### 3. Experimental Section

#### 3.1. General Remarks

All manipulations were performed in an inert atmosphere using a standard glove box and Schlenk techniques. CH<sub>2</sub>Cl<sub>2</sub> and acetonitrile were stirred over CaH<sub>2</sub> and transferred to the reservoir under vacuum. Toluene, hexane, diethyl ether and THF were distilled from benzophenone ketyl. Methylcyclohexane (anhydrous grade) used for the oligomerization reactions was purchased from Aldrich and purified over a Na/K alloy. Ethylene was purified by contact with molecular sieves and copper for more than 12 h under a pressure of 48 bar. The <sup>1</sup>H NMR (600 MHz), <sup>13</sup>C NMR (150 MHz) and <sup>31</sup>P NMR (243 MHz) spectra were

recorded using a JEOL ECZ 600 spectrometer. Gas-chromatography with flame-ionization detection (GC-FID) analysis was performed using a YL6500 GC system equipped with an HP-PONA (50 m × 0.200 mm × 0.50 μm) column.  $[\text{CrCl}_2(\text{NCCH}_3)_4]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  and  $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$  were prepared according to previously reported methods [48].

### 3.2. (1-Octyl)<sub>3</sub>SiCl

(1-Octyl)<sub>3</sub>SiH (18.3 g, 49.6 mmol) and FeCl<sub>3</sub> (0.0805 g, 0.496 mmol, 1mol%) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (70 mL) and acetyl chloride (4.28 g, 54.6 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (9 mL) was added dropwise. After stirring for 1 d, all volatiles were removed using a vacuum line. The residue was dissolved in hexane (90 mL), and the insoluble fractions were removed by Celite-aided filtration. Removal of the solvent afforded a yellow oil (19.9 g, 99%), which was used for the next step without further purification. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>): δ 1.49 (quintet, *J* = 7.8 Hz, 6H, CH<sub>2</sub>), 1.40–1.18 (30H, CH<sub>2</sub>), 0.91 (t, *J* = 6.6 Hz, 9H, CH<sub>3</sub>), 0.87–0.78 (br, 6H, SiCH<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, C<sub>6</sub>D<sub>6</sub>): δ 33.7, 32.4, 29.7, 29.7, 23.5, 23.1, 16.7, 14.4 ppm.

### 3.3. BrC<sub>6</sub>H<sub>4</sub>-*p*-Si(1-octyl)<sub>3</sub>

1,4-Dibromobenzene (6.63 g, 28.1 mmol) was dissolved in THF (70 mL). After cooling to −78 °C, nBuLi (10.2 mL, 2.50 M in hexane, 25.5 mmol) was added dropwise. The resulting solution was stirred at −78 °C for 2 h, and then (1-octyl)<sub>3</sub>SiCl (10.0 g, 24.8 mmol) dissolved in THF (14 mL) was added dropwise. The solution was allowed to warm to room temperature and then stirred at room temperature for 2 h. After all volatiles were removed using a vacuum line, the residue was treated with hexane (30 mL). The insoluble fractions were removed by Celite-aided filtration, and the solvent was removed using a rotary evaporator. The residue was dissolved in hexane (60 mL), and the resulting solution was passed through a short pad of silica gel (13 g). Removal of the solvent afforded a colorless oil, which was evacuated at 70 °C to remove unreacted 1,4-dibromobenzene (yield 11.7 g, 90%). <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.26 (d, *J* = 8.4 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 7.23 (d, *J* = 7.8 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 1.44–1.34 (12H, CH<sub>2</sub>), 1.34–1.21 (24H, CH<sub>2</sub>), 0.91 (t, *J* = 7.2 Hz, 9H, CH<sub>3</sub>), 0.85–0.78 (br, 6H, SiCH<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, C<sub>6</sub>D<sub>6</sub>): δ 137.0, 136.1, 131.4, 124.1, 34.3, 32.4, 29.8, 29.7, 24.2, 23.2, 14.4, 12.7 ppm.

### 3.4. Et<sub>2</sub>NP[C<sub>6</sub>H<sub>4</sub>-*p*-Si(1-octyl)<sub>3</sub>]<sub>2</sub>

BrC<sub>6</sub>H<sub>4</sub>-*p*-Si(1-octyl)<sub>3</sub> (13.1 g, 25.1 mmol) was dissolved in a mixed solvent of diethyl ether (41 mL) and toluene (98 mL). After cooling to −30 °C, nBuLi (13.0 mL, 2.50 M in hexane, 32.6 mmol) was added dropwise. The solution was allowed to warm to room temperature and then stirred for 2 h. All volatiles were completely removed using a vacuum line. THF (135 mL) was added and the resulting solution was cooled to −30 °C. Et<sub>2</sub>NPCl<sub>2</sub> (2.29 g, 13.2 mmol) dissolved in THF (13 mL) was added dropwise. The solution was allowed to warm to room temperature and stirred for 2 h. After the solvent was removed using a vacuum line, the residue was treated with hexane (190 mL). The insoluble fractions were removed by Celite-aided filtration, and the resulting solution was passed through a short pad of silica gel (12.4 g). Removal of the solvent afforded a light yellow oil (9.14 g, 74%), which was used for the next step without further purification. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.64 (t, <sup>3</sup>*J*<sub>P-H</sub> = 7.2 Hz, 4H, C<sub>6</sub>H<sub>4</sub>), 7.59 (d, *J* = 7.8 Hz, 4H, C<sub>6</sub>H<sub>4</sub>), 3.09 (q, *J* = 6.6 Hz, 2H, NCH<sub>2</sub>CH<sub>3</sub>), 3.07 (q, *J* = 6.6 Hz, 2H, NCH<sub>2</sub>CH<sub>3</sub>), 1.49 (m, 12H, CH<sub>2</sub>), 1.40 (quintet, *J* = 7.2 Hz, 12H, CH<sub>2</sub>), 1.36–1.23 (48H, CH<sub>2</sub>), 0.97–0.91 (br, 12H, SiCH<sub>2</sub>), 0.92 (t, *J* = 7.2 Hz, 18H, CH<sub>3</sub>), 0.89 (t, *J* = 7.2 Hz, 6H, NCH<sub>2</sub>CH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, C<sub>6</sub>D<sub>6</sub>): δ 141.8 (d, <sup>1</sup>*J*<sub>P-C</sub> = 15.8 Hz), 138.3, 134.3, 131.8 (d, <sup>3</sup>*J*<sub>P-C</sub> = 18.6 Hz), 44.9 (d, <sup>2</sup>*J*<sub>P-C</sub> = 15.9 Hz), 34.3, 32.4, 29.8, 29.7, 24.4, 23.2, 14.7 (d, <sup>3</sup>*J*<sub>P-C</sub> = 2.9 Hz), 14.4, 13.0 ppm. <sup>31</sup>P (243 MHz, C<sub>6</sub>D<sub>6</sub>): 62.1 ppm.

### 3.5. $\text{ClP}[\text{C}_6\text{H}_4\text{-}p\text{-Si(1-octyl)}_3]_2$

$\text{PCl}_3$  (9.48 g, 69.0 mmol) was added to a flask containing  $\text{Et}_2\text{NP}[\text{C}_6\text{H}_4\text{-}p\text{-Si(1-octyl)}_3]_2$  (9.14 g, 9.22 mmol) and the resulting solution was refluxed for 2 h under  $\text{N}_2$  atmosphere. The remaining  $\text{PCl}_3$  and generated  $\text{Et}_2\text{NPCL}_2$  were removed by vacuum distillation at  $80^\circ\text{C}$ . The residue was dissolved in hexane (53 mL), and the insoluble fractions were removed by Celite-aided filtration. Removal of the solvent afforded a light-yellow oil, which was used for the next step without further purification.  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.68 (t,  $^3J_{\text{P-H}} = 7.8$  Hz, 4H,  $\text{C}_6\text{H}_4$ ), 7.49 (d,  $J = 7.2$  Hz, 4H,  $\text{C}_6\text{H}_4$ ), 1.45–1.34 (24H,  $\text{CH}_2$ ), 1.34–1.24 (48H,  $\text{CH}_2$ ), 0.92 (t,  $J = 7.2$  Hz, 18H,  $\text{CH}_3$ ), 0.89–0.83 (br, 12H,  $\text{SiCH}_2$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  141.4, 139.9 (d,  $^1J_{\text{P-C}} = 33$  Hz), 134.7 (d,  $^3J_{\text{P-C}} = 5.7$  Hz), 131.5 (d,  $^2J_{\text{P-C}} = 24.5$  Hz), 34.3, 32.4, 29.8, 29.7, 24.3, 23.2, 14.4, 12.8 ppm.  $^{31}\text{P}$  (243 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  82.7 ppm.

### 3.6. $i\text{PrN}(\text{PAR}_2)_2$ ( $\text{Ar} = -\text{C}_6\text{H}_4\text{-}p\text{-Si(1-octyl)}_3$ )

$i\text{PrNH}_2$  (0.280 g, 4.75 mmol) dissolved in  $\text{CH}_2\text{Cl}_2$  (37 mL) was added dropwise to a flask containing  $\text{ClPAR}_2$  ( $\text{Ar} = -\text{C}_6\text{H}_4\text{-}p\text{-Si(1-octyl)}_3$ ) (9.96 g, 10.4 mmol) and  $\text{Et}_3\text{N}$  (4.80 g, 47.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (62 mL). The resulting solution was stirred overnight at room temperature, and all volatiles were removed using a vacuum line. The residue was treated with hexane (73 mL), and the insoluble fractions were removed by Celite-aided filtration. Silica gel (13.5 g), which had been treated beforehand with hexane/ $\text{Et}_3\text{N}$  (*v/v*, 50:1), was added to the filtrate. After stirring for 30 min, the mixture was filtered. Removal of the solvent afforded a light yellow oil (8.81 g, 98%), which was used without further purification.  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  8.10–7.27 (br, 8H,  $\text{C}_6\text{H}_4$ ), 7.56 (d,  $J = 6.6$  Hz, 8H,  $\text{C}_6\text{H}_4$ ), 3.90 (m, 1H,  $\text{NCHCH}_3$ ), 1.51 (quintet,  $J = 7.8$  Hz, 24H,  $\text{CH}_2$ ), 1.44 (quintet,  $J = 7.2$  Hz, 24H,  $\text{CH}_2$ ), 1.40–1.19 (96H,  $\text{CH}_2$ ), 1.27 (d,  $J = 6.6$  Hz, 6H,  $\text{NCHCH}_3$ ), 0.94 (t,  $J = 7.2$  Hz, 36H,  $\text{CH}_3$ ), 0.95 (br, 24H,  $\text{SiCH}_2$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  141.8–140.9 (br), 138.9, 134.3 (d,  $^3J_{\text{P-C}} = 5.9$  Hz), 133.2–132.4 (br), 52.5 (t,  $^2J_{\text{P-C}} = 10.1$  Hz), 31.4, 32.4, 29.8, 29.8, 24.6 (quintet,  $^3J_{\text{P-C}} = 7.2$  Hz), 24.4, 23.2, 22.8 ppm.  $^{31}\text{P}$  (243 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  55.4, 42.1 ppm.

### 3.7. Preparation of $[i\text{PrN}(\text{PAR}_2)_2-\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ Using $[\text{CrCl}_2(\text{NCCH}_3)_4]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$

To a flask containing  $i\text{PrN}(\text{PAR}_2)_2$  ( $\text{Ar} = -\text{C}_6\text{H}_4\text{-}p\text{-Si(1-octyl)}_3$ ) (1.41 g, 0.742 mmol) in  $\text{CH}_2\text{Cl}_2$  (9 mL) was added  $[\text{CrCl}_2(\text{NCCH}_3)_4]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  (0.716 g, 0.742 mmol) dissolved in  $\text{CH}_2\text{Cl}_2$  (3 mL). After stirring at room temperature for 2.5 h, the solvent was removed using a vacuum line to obtain a bright green viscous oil (1.98 g, 99% based on the formula  $[\text{3-CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ). The residue was dissolved in methylcyclohexane (196 g) to make a 1.0-wt% solution, which was used for the tetramerization reactions.

### 3.8. Attempt to Prepare $[i\text{PrN}(\text{PAR}_2)_2-\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ Using $[\text{PhN}(\text{H})\text{Me}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ and $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$

$i\text{PrN}(\text{PAR}_2)_2$  ( $\text{Ar} = -\text{C}_6\text{H}_4\text{-}p\text{-Si(1-octyl)}_3$ ) (0.500 g, 0.264 mmol) dissolved in  $\text{CH}_2\text{Cl}_2$  (4.5 mL) was added to a slurry of  $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$  (0.0800 g, 0.260 mmol Cr) in  $\text{CH}_2\text{Cl}_2$  (2 mL). Upon the addition, the  $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$  was completely dissolved, affording a blue solution. After stirring for 2 h,  $[\text{PhN}(\text{H})\text{Me}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  (0.211 g, 0.264 mmol) dissolved in  $\text{CH}_2\text{Cl}_2$  (1.0 mL) was added dropwise. Upon addition, the color of the solution changed from blue to blue-green. After stirring for 1 h, all volatiles were completely removed using a vacuum line. The residue was treated with methylcyclohexane (75.0 g), and the resulting solution was stirred overnight. The insoluble fractions were removed using Celite-aided filtration. The solution was used for tetramerization reactions.

### 3.9. $[\text{CrCl}_2(\text{NCCH}_3)_4]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$

2,2-Dimethoxypropane (45.7 g, 452 mmol) was added to a flask containing  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (9.30 g, 34.9 mmol). Initially,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  was insoluble in 2,2-dimethoxypropane, but a purple solution was obtained after stirring for 4 h. The volatiles were removed using a vacuum line to obtain a brown, gummy residue. 2,2-Dimethoxypropane (45.7 g, 452 mmol) was added again and the mixture stirred at  $70^\circ\text{C}$  for 1.5 h to precipitate green solids, which

were collected by filtration and washed with 2,2-dimethoxypropane (17 mL). The isolated solids were dried under vacuum to obtain  $[(\text{MeOH})_4\text{CrCl}_2]^+\text{Cl}^-$  (9.4 g, 94%) [49]. The prepared  $[(\text{MeOH})_4\text{CrCl}_2]^+\text{Cl}^-$  (2.39 g, 8.35 mmol) was dissolved in EtOH (38 mL), and  $\text{K}^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  (6.00 g, 8.35 mmol) dissolved in EtOH (38 mL) was added to the resulting solution. A white solid (KCl) precipitated immediately and was removed by Celite-aided filtration. Volatiles in the filtrate were removed using a vacuum line. The residue was dissolved in acetonitrile (12 mL), and the resulting solution was heated to 60 °C with heat gun. The volatiles were removed using a vacuum line while heated with heat gun. This procedure of dissolution in acetonitrile and solvent removal was repeated five times more time. Finally, the residue was dissolved in acetonitrile (12 mL) and the resulting solution was stored at −30 °C, resulting in the precipitation of a green solid (6.46 g). Solvent was removed from the mother liquor, and the residue was dissolved in acetonitrile (2.2 mL). Storing the solution at −30 °C precipitated the second crops (0.670 g, total yield 88%). The isolated solid (14.0 mg) and 9-methylanthracene (10.0 mg) as an external standard were dissolved in THF- $d_8$ , and the  $^1\text{H}$  NMR spectrum was recorded. Integration values at 1.94 ppm ( $\text{CH}_3\text{CN}$  signal) and 3.08 ppm (methyl signal in the external standard) agreed with the formula  $[\text{CrCl}_2(\text{NCCH}_3)_{4.02}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ .

### 3.10. Ethylene Tetramerization

Methylcyclohexane (200 mL) was placed in a bomb reactor, and after the temperature was raised to 40 °C,  $i\text{Bu}_3\text{Al}$  (0.149 g, 750  $\mu\text{mol}$ ) and  $[\mathbf{3}-\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  (7.55 mg, 1.0 wt% solution in methylcyclohexane, 2.8  $\mu\text{mol}$ ) were successively added. The reactor was immediately charged with ethylene gas to a pressure of 35 bar. The temperature was controlled at 40 °C, and ethylene gas was continuously fed to maintain the pressure at 35 bar. The oligomerization was allowed to proceed for 30 min, and the ethylene gas was then vented off. The weight percentages of the oligomers generated (1-octene (1-C8), 1-hexene (1-C6), methylcyclopentane + methylenecyclopentane (cy-C6) and higher oligomers above C10 (>C10)) were calculated from the analysis of GC data, using nonane as an external standard. The solid PEs generated were isolated by filtration at room temperature.

## 4. Conclusions

By replacing the  $-\text{Ph}$  groups in the conventional PNP ligand ( $i\text{PrN}(\text{PPh}_2)_2$ ) with  $-\text{C}_6\text{H}_4-p\text{-SiR}_3$  ( $\text{R} = n\text{Bu}$ , 1-hexyl, 1-octyl, 2-ethylhexyl, 3,7-dimethyloctyl), the formation of inactive Cr species coordinated by two PNP ligands, i.e.,  $[(\text{PNP})_2-\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ , was prevented, and highly active  $[(\text{PNP})-\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  type complexes were generated in the reaction between  $i\text{PrN}(\text{PAR}_2)_2$  and  $[(\text{CH}_3\text{CN})_4\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ . Among the Cr complexes prepared, the one bearing  $-\text{Si}(1\text{-octyl})_3$  substituents (i.e.,  $[i\text{PrN}(\text{PAR}_2)_2\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ,  $\text{Ar} = -\text{C}_6\text{H}_4-p\text{-Si}(1\text{-octyl})_3$ ) showed extremely high activity (11,100 kg/g-Cr/h, 100 kg/g-catalyst) when combined with common  $i\text{Bu}_3\text{Al}$ , avoiding the use of expensive MMAO. Moreover, the 1-octene selectivity was as high as 75.0 wt% at 40 °C under 35 bar ethylene pressure, and the undesired >C10 fraction was generated in the least amount (10.7 wt%). A 10 g-scale synthesis of the ligand  $i\text{PrN}(\text{PAR}_2)_2$  ( $\text{Ar} = -\text{C}_6\text{H}_4-p\text{-Si}(1\text{-octyl})_3$ ) was demonstrated, and a facile and low-cost preparation method for the Cr precursor  $[(\text{CH}_3\text{CN})_4\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  was also developed, aimed at the commercial production of 1-octene with the prepared Cr catalyst.

## 5. Patent

A patent was applied on this study (Kr 10-2003-0316372, 22 January 2021, assigned to Hanwha Total).

**Supplementary Materials:** The following are available online at <https://www.mdpi.com/article/10.3390/catal11091122/s1>, Figures S1–S3:  $^{31}\text{P}$  NMR spectra of bis (phosphine) ligands,  $\text{Et}_2\text{NP}(\text{C}_6\text{H}_4\text{-}p\text{-SiR}_3)_2$  and  $\text{CIP}(\text{C}_6\text{H}_4\text{-}p\text{-SiR}_3)_2$ , Figures S4, S5:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of  $\text{HSiR}_3$ , Figures S6–S8:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of  $\text{ClSiR}_3$ , Figures S9–S12:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of  $\text{BrC}_6\text{H}_4\text{-}p\text{-SiR}_3$ , Figures S13–S16:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of  $\text{Et}_2\text{NP}(\text{C}_6\text{H}_4\text{-}p\text{-SiR}_3)_2$ , Figures S17–S20:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of  $\text{CIP}(\text{C}_6\text{H}_4\text{-}p\text{-SiR}_3)_2$ , Figures S21–S24:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of  $\text{iPrN}(\text{PAR}_2)_2$  ( $\text{Ar} = \text{-C}_6\text{H}_4\text{-}p\text{-SiR}_3$ ), Figure S25:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra  $\text{C}_6\text{H}_{11}\text{N}(\text{PAR}_2)_2$  ( $\text{Ar} = \text{-C}_6\text{H}_4\text{-}p\text{-Si}(\text{1-octyl})_3$ ), Figure S26:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of  $2\text{-Et-6-Me-C}_6\text{H}_3\text{N}(\text{PAR}_2)_2$  ( $\text{Ar} = \text{-C}_6\text{H}_4\text{-}p\text{-Si}(\text{nBu})_3$ ), Figure S27:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of  $\text{iPrN}(\text{H})\text{PAR}_2$  ( $\text{Ar} = \text{-C}_6\text{H}_4\text{-}p\text{-Si}(\text{1-decyl})_3$ ), Figure S28:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of  $\text{iPrN}(\text{PPh}_2)(\text{PAR}_2)$  ( $\text{Ar} = \text{-C}_6\text{H}_4\text{-}p\text{-Si}(\text{1-decyl})_3$ ), Figure S29:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of *ortho*- $\text{C}_6\text{H}_4\text{N}(\text{PPh}_2)(\text{PAR}_2)$  ( $\text{Ar} = \text{-C}_6\text{H}_4\text{-}p\text{-Si}(\text{1-octyl})_3$ ).

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