Methyaluminoxane-Free Chromium Catalytic System for Ethylene Tetramerization

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Supporting Information

ABSTRACT: Ethylene tetramerization catalyst systems comprising a Cr(III) complex containing PNP ligands and methyaluminoxane (MAO) are useful for the production of 1-octene. However, a concern with these systems is the use of expensive MAO in excess. Herein, we report a catalytic system that avoids the use of MAO. Metathesis of CrCl3(THF)3 and [(CH3CN)4Ag]+[B(C6F5)4]− afforded [L4CrCl2(THF)]+[B(C6F5)4]− (L = CH3CN or tetrahydrofuran (THF)), which was converted to [(PNP)CrCl2L2][B(C6F5)4]−, where PNP is iPrN(PPh2)2 (1) or [CH2(CH2)16]2CHN(PPh2)2 (2). The molecular structures of [(THF)2CrCl3][B(C6F5)4]− and [1-CrCl3(THF)]2[B(C6F5)4]− were unambiguously determined by X-ray crystallography. The cationic (PNP)CrIII complexes paired with [B(C6F5)4]− anions, that is, [(PNP)CrCl2(CH3CN)]+[B(C6F5)4]−, exhibited high activity in chlorobenzene when activated with common trialkylaluminum species (Me3Al, Et3Al, and iBu3Al). The activities and selectivity were comparable to those of the original MAO-based Sasol system ([CrCl3/MAO]). When activated with Et3Al or iBu3Al, the Cr complex, [2-CrCl2(CH3CN)]+[B(C6F5)4]−, which bears long alkyl chains, showed high activity in the more desirable methycyclohexane solvent (89 kg/g-Cr/h) and much higher activity in cyclohexene (168 kg/g-Cr/h). Other advantages of the [2-CrCl2(CH3CN)]+[B(C6F5)4]−/Et3Al system in cyclohexene were negligible catalyst deactivation, formation of only a negligible amount of polyethylene side product (0.3%), and formation of fewer unwanted side products above C10. The [B(C6F5)4]− anion is compatible with trialkylaluminum species once it is not paired with a trityl cation. Hence, [(PNP)CrCl2(CH3CN)]+[B(C6F5)4]−/Et3Al exhibited a significantly higher activity than that of a previously reported system composed of [Ph3C]+[B(C6F5)4]−, that is, 1/CrCl3(THF)/[Ph3C]+[B(C6F5)4]−/Et3Al.

INTRODUCTION

Production of linear α-olefins (LAOs) through ethylene oligomerization is an important issue in both industry and academia.1−6 and development of efficient catalysts for this process is an active research area.7−22 LAOs are used in the polyolefin industry as comonomers, and demand for them has increased with the increase in polyolefin production using the homogeneous metallocene-type catalysts. Recently, LAOs have also been used in the production of poly(α-olefin) lubricant base-stocks.23 LAOs can be separated from wide-distribution mixtures of 1-alkenes that are produced using nickel catalysts via the Shell higher olefin process.24,25 Catalysts that can selectively generate 1-hexene or 1-octene from ethylene have also been discovered. For example, a trimerization catalyst composed of pyrrole, (2-ethylhexanoate)Cr(III), and an alkylaluminoxane reagent (Et3Al + Et2AlCl) was discovered at Phillips in the early 1990s,26−28 and a tetramerization catalyst composed of iPrN(PPh2)2 (1), Cr(acac)3, and methyaluminoxane (MAO) was discovered at Sasol in the early 2000s.29−33 There is some controversy concerning the active species in these selective oligomerization catalysts. Electron paramagnetic resonance (EPR) studies showed that the majority of CrIII precursors were converted to EPR-silent CrII by the action of the alkylaluminoxane cocatalyst.34−36 On the basis of this observation, a catalytic cycle involving the CrII/IV species was proposed,37,38 but a catalytic cycle involving the cationic CrI/III species paired with a MAO-derived noncoordinating anion is currently more generally accepted (Scheme 1).34,35,38−40

Scheme 1. Active Species Proposed for Ethylene Tetramerization, and the CrIII Complexes Targeted in This Work

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recently prepared various zwitterionic CrII complexes, but none of them were active in ethylene oligomerization, convincing us of the validity of the catalytic cycle involving cationic CrII/III species.41

Although the Phillips system requires inexpensive alkylaluminum Et3Al and Et2AlCl as an activator, the use of expensive MAO in excess (Al/Cr, 300–500) is a critical concern when considering the commercial application of the Sasol system. A catalytic system containing [Ph3C]+[B(C6F5)4]− instead of MAO (i.e., 1-CrIIICl2/[Ph3C]+[B(C6F5)4]−/Et3Al) was proposed on the basis of the aforementioned catalytic cycle involving cationic CrII/III species, but its activity was significantly inferior to that of the MAO-derived system and resulted in the generation of a large amount of polyethylene (PE).42 Its failure was attributed to the instability of [B(C6F5)4]− anions, and efforts were made to develop other types of noncoordinating anions, leading to the development of catalytic systems containing [Al(OC(CF3)3)4]− anions, which showed high activity even in the solid phase. Similarly, it has been reported that reacting [L4CrCl2]+[Al(OC(CF3)3)4]− with AgNO3 in acetonitrile.50,51 In this work, we prepared cationic CrIII complexes paired with [B(C6F5)4]− anions. However, their preparations were not targeted toward ethylene oligomerization.46–49

### RESULTS AND DISCUSSION

#### Preparation of Cationic CrIII Complexes

Our synthetic strategy for the targeted complexes ([PnP]CrIII)2Cl2][B(C6F5)4]− was to react [L4CrCl2][B(C6F5)4]− (L = CH3CN or tetrahydrofuran (THF)) with PNP ligands (Scheme 2a). The key complex in this synthetic scheme, [(CH3CN)4CrIIICl2][B(C6F5)4]−, was prepared by the metathesis of CrCl3(THF)3 and [(CH3CN)4Ag][B(C6F5)4]− in acetonitrile. The silver complex, [(CH3CN)4CrIIICl2][B(C6F5)4]−, was easily prepared by reacting commercially available CrCl3(THF)3 and [(CH3CN)4Ag][B(C6F5)4]−. Herein, avoiding the use of highly reactive [Ph3C]+[B(C6F5)4]− anions, we prepared cationic CrIII complexes paired with common [B(C6F5)4]− anions, which showed high activity even when activated with a common trialkylaluminum agent (Scheme 1).52 There have been several previous reports of cationic CrIII complexes paired with [B(C6F5)4]− anions. However, their preparations were not targeted toward ethylene oligomerization.46–49
insoluble in hydrocarbon solvents. However, it is soluble in more polar chlorobenzene or CH2Cl2.

Aliphatic hydrocarbon solvents (e.g., methylcyclohexane) are the best options for commercial ethylene tetramerization. Hence, complexes soluble in methylcyclohexane are desirable. A PNP ligand bearing long alkyl chains ([CH3(CH2)16]2CHN-(PPh2)2, 2 in Scheme 2) was prepared in good yield (70%) by the conventional synthetic method, that is, reacting Ph2PCl with a long-chain alkyl amine [CH3(CH2)16]2CHNH2 in the presence of excess triethylamine.29 The alkyl amine, [CH3(CH2)16]2CHNH2, was prepared from inexpensive 18-pentatricontanone ([CH3(CH2)16]2C=O).54,55 The long-chain PNP ligand is highly soluble in hexane. PNP ligand 2 was reacted with [(CH3CN)4CrIIICl2]+[B(C6F5)4]− in CH2Cl2. To minimize (or avoid) generation of undesired bis(PNP)CrIII species, the mole ratio of the reactants was set at 1:2. A green species was extracted from the reaction mixture using hot methylcyclohexane (ca. 50 °C) while leaving [(CH3CN)4CrIIICl2]+[B(C6F5)4]−, which remained owing to its addition in excess, in the solid phase. The extracted species was assigned as the desired mono(PNP)CrIII complex [2-CrCl2(CH3CN)2]+[B(C6F5)4]− on the basis of its green color and elemental analysis data and was used for oligomerization studies. The complex is clearly soluble in hydrocarbon solvents bearing π-electrons such as toluene or cyclohexene, even at room temperature.

Figure 1. Thermal ellipsoid plots (30% probability level) of [(CH3CN)4Ag]+[B(C6F5)4]− (a), [(THF)4CrCl2]+[B(C6F5)4]− (b), and (o-Me2NC6H4CH2)3Cr (c). Selected bond distances (Å) and angles (deg) are as follows: In (a), Ag−N(1), 2.311(4); Ag−N(2), 2.293(4); Ag−N(3), 2.247(3); Ag−N(4), 2.323(3); N(1)−Ag−N(2), 120.99(11); N(3)−Ag−N(4), 135.82(10); N(2)−Ag−N(3), 102.70(11); N(1)−Ag−N(3), 106.56(10); C−N(1)−Ag, 170.1(3); C−N(2)−Ag, 172.1(3); C−N(3)−Ag, 177.9(2); C−N(4)−Ag, 155.7(3); angle between the N(1)−Ag−N(2) and N(3)−Ag−N(4) planes, 85.04(6). In (b), Cr−O(1), 2.002(3); Cr−O(2), 2.004(3); Cr−Cl(1), 2.2978(10); O(1)−Cr−O(1)′, 180; O(1)−Cr−O(1)′, 180; Cl(1)−Cr−O(1), 90; Cl(1)−Cr−O(2), 90; O(1)−Cr−O(2), 90. In (c), Cr−N(1), 2.4413(14); Cr−P(1), 2.4413(14); Cr−P(2), 2.4844(15); Cr−O(1), 2.027(3); Cr−O(2), 2.057(3); Cl(1)−Cr−Cl(2), 179.59(7); P(1)−Cr−P(2), 66.85(5); P(1)−N−P(2), 106.0(2).

Figure 2. Thermal ellipsoid plots (30% probability level) of [1-CrCl2(THF)2][B(C6F5)4]− (a) and [1-CrCl2][B(C6F5)4]− (b).

Selected bond distances (Å) and angles (deg) are as follows. In (a), Cr−Cl(1), 2.2799(15); Cr−Cl(2), 2.2869(15); Cr−P(1), 2.4413(14); Cr−P(2), 2.4844(15); Cr−O(1), 2.027(3); Cr−O(2), 2.057(3); Cl(1)−Cr−Cl(2), 179.59(7); P(1)−Cr−P(2), 66.85(5); P(1)−N−P(2), 106.0(2). In (b), Cr−Cl(1), 2.2872(7); Cr−Cl(2), 2.273(2); Cr−P(1), 2.485(2); Cr−P(2), 2.454(2); Cr−P(3), 2.454(2); Cr−P(4), 2.464(2); Cl(1)−Cr−Cl(2), 171.9(7); P(1)−Cr−P(2), 66.90(8); P(1)−N(1)−P(2), 105.6(4).
Preparation of the cationic (PNP)CrIII complex containing an ortho-dimethylaminobenzyl ligand instead of chloride was attempted (Scheme 2b). The starting Cr-precursor, (o-Me2NC6H4CH2)3Cr, was prepared by reacting CrCl3(THF)2 with o-Me2NC6H4CH2Li. The pure complex was isolated by recrystallization in CH2Cl2 at 30 °C. The 1H NMR spectrum, signals assignable to -Me2NC6H4CH2 are almost linear (170.1(3), 172.1(3), and 177.9(2)°), whereas the two chloride ligands are situated at the axial sites in the CrIII center. On the basis of these observations, the generated complex was assigned as [(o-Me2NC6H4CH2)3CrIII(THF)2]2[B(C6F5)4]−. All attempts to grow single crystals of this complex were unsuccessful and, furthermore, the color of the solution changed during the recrystallization process, indicating that it is unstable. Thus, PNP ligand 1 was subsequently added to the CD2Cl2 solution containing the unpurified [(o-Me2NC6H4CH2)3CrIII(THF)2]2[B(C6F5)4]−. In the 1H NMR spectrum, the signals for 1 are absent, indicating the coordination of the PNP ligand to the paramagnetic CrIII center (Figure S7). Broad diethyl ether signals are observed at 3.78 and 1.54 ppm after overnight reaction. These observations positively indicate the generation of the desired complex [1-Cr(CH2C6H4NMe2)2][B(C6F5)4]−. Attempts to grow single crystals of this species were also unsuccessful. Using the long-chain PNP ligand (2), a methylcyclohexane-soluble complex was prepared by the same procedure, which was tentatively assigned as [2-Cr(CH2C6H4NMe2)3][B(C6F5)4]− and used for the oligomerization studies.

**X-ray Crystallographic Studies.** Single crystals of [(CH3CN)4Ag][B(C6F5)4]− for X-ray crystallography were grown in acetonitrile solution at −30 °C. Tetrahedral coordination of the CH3CN ligands to silver is observed with no direct chemical bonding between [(CH3CN)4Ag]− and [B(C6F5)4]− (Figure 2a). One Ag=−N−C bond angle deviates significantly from linearity (155.7(3)°), whereas the other three are almost linear (170.1(3), 171.2(3), and 177.9(2)°). Single crystals of [(THF)2CrCl2][B(C6F5)4]− were grown in THF at −30 °C after the acetonitrile ligands in [(CH3CN)4Ag][B(C6F5)4]− were replaced with THF. The CrIII center adopts perfect octahedral geometry surrounded by two chloride and four THF ligands (Figure 2b). The four THF ligands form a plane with the Cr center, whereas the two chloride ligands are situated at the axial sites in trans configuration. The oxygen atoms in THF adopt sp2 hybridization, that is, the sum of bond angles around O is 360°, indicating π-donation from O to the CrIII center. The structure of (o-Me2NC6H4CH2)3Cr is shown in Figure 1c. The Cr center adopts distorted octahedral geometry with facial arrangement of three benzyl CH2 groups and three amine ligands. The plain formed by the three carbon ligands is parallel to the planes, 0.90(6)° exposed, making it very accessible for the attack by [H(OEt2)3][B(C6F5)4]−.

**Table 1. Ethylene Oligomerization Results**

| entry | solvent | catalyst | activator | activity (kg/g-Cr/h) | 1-C6 (wt %) | cy-C6 (wt %) | 1-C8 (wt %) | >C10 (wt %) | PE (wt %) |
|-------|---------|----------|-----------|---------------------|-------------|-------------|-------------|-------------|----------|
| 1     | C6H10   | [1-CrCl]2[B(C6F5)4]− | Me3Al | 155 | 41.6 | 2.4 | 43.7 | 9.4 | 2.2 |
| 2     | C6H10   | [1-CrCl]2[B(C6F5)4]− | Me3Al | 50 | 30.4 | 3.4 | 61.3 | 3.2 | 1.1 |
| 3     | C6H10   | [1-CrCl]2[B(C6F5)4]− | iBu3Al | 74 | 30.7 | 2.2 | 47.2 | 8.2 | 1.7 |
| 4     | C6H10   | [1-CrCl]2[B(C6F5)4]− | iBu3Al | 126 | 31.3 | 2.5 | 45.8 | 9.7 | 10.6 |
| 5     | C6H10   | [1-CrCl]2[B(C6F5)4]− | iBu3Al | 288 | 44.3 | 2.3 | 40.1 | 12.2 | 0.7 |
| 6     | C6H10   | [1-CrCl]2[B(C6F5)4]− | Et3Al | 224 | 44.3 | 2.3 | 40.6 | 11.4 | 1.3 |
| 7     | C6H10   | [1-CrCl]2[B(C6F5)4]− | iBu3Al | 221 | 37.5 | 2.1 | 46.6 | 12.6 | 1.0 |
| 8     | C6H10   | 1-CrCl3 | MMAO6 | 203 | 44.9 | 2.2 | 39.6 | 11.3 | 1.2 |
| 9     | C6H10   | [2-CrCl]2[B(C6F5)4]− | Me3Al | 140 | 50.2 | 2.1 | 37.3 | 8.7 | 1.6 |
| 10    | MeC6H11 | [1-CrCl]2[B(C6F5)4]− | Et3Al | 13 | 8.4 | 3.1 | 53.5 | 30.6 | 3.7 |
| 11    | MeC6H11 | [1-CrCl]2[B(C6F5)4]− | iBu3Al | 26 | 10.5 | 4.5 | 68.0 | 14.9 | 1.3 |
| 12    | MeC6H11 | [2-CrCl]2[B(C6F5)4]− | Et3Al | 77 | 13.6 | 4.9 | 71.3 | 8.2 | 1.4 |
| 13    | MeC6H11 | [2-CrCl]2[B(C6F5)4]− | iBu3Al | 84 | 14.3 | 4.7 | 70.3 | 9.4 | 1.0 |
| 14    | MeC6H11 | [2-CrCl]2[B(C6F5)4]− | iBu3Al | 89 | 13.8 | 4.8 | 70.9 | 9.4 | 0.4 |
| 15    | MeC6H11 | [2-Cr(CH2C6H4NMe2)2][B(C6F5)4]− | (iBu3Al)O | 29 | 20.8 | 3.2 | 44.5 | 11.2 | 8.0 |
| 16    | MeC6H11 | 1 + Cr(acac)3 | MMAO6 | 163 | 7.9 | 4.6 | 72.7 | 13.1 | 1.3 |
| 17    | MeC6H11 | [2-CrCl]2[B(C6F5)4]− | iBu3Al | 65 | 8.1 | 3.1 | 58.4 | 8.5 | 0.8 |
| 18    | C6H10   | [2-CrCl]2[B(C6F5)4]− | iBu3Al | 168 | 15.2 | 4.9 | 74.1 | 5.3 | 0.3 |
| 19    | C6H10   | [2-CrCl]2[B(C6F5)4]− | Et3Al | 168 | 14.2 | 4.9 | 71.7 | 7.5 | 0.1 |
| 20    | C6H10   | [2-CrCl]2[B(C6F5)4]− | Et3Al | 160 | 14.2 | 4.9 | 71.6 | 8.0 | 0.3 |
| 21    | C6H10   | 1 + Cr(acac)3 | MMAO6 | 257 | 10.1 | 4.7 | 73.1 | 8.3 | 0.9 |

*aOligomerization conditions: Cr complex: 1.5 μmol; Al/Cr: 300; solvent: 20 mL; temperature: 75 °C for entries 1–9, 45 °C for entries 10–21; ethylene: 30 bar for entries 1–9, 45 bar for entries 10–21, 30 min. Modified MAO sourced from Akzo Nobel (MMAO-3A 7.0 Al wt % in heptane). DOI: 10.1021/acsomega.6b00506*
complex, \( \text{[1,2-CrCl}_2\text{]}^+\text{[B(C_F_3)_4]}^- \). Both complexes exhibit distorted octahedral coordination. The PNP and the two THF ligands form a plane with the CrIII center (the angle between the \( \text{P-Cr-P} \) and \( \text{O-Cr-O} \) planes, 4.02(9°) in the former case, and the two PNP ligands form a rather distorted plane with the CrIII center in the latter case (the angle between the \( \text{P(1)-Cr-P(2)} \) and \( \text{P(3)-Cr-P(4)} \) planes, 8.52(7°)). The two chlorides occupy the axial sites almost linearly (the \( \text{Cl-Cr-Cl} \) angles, 179.59(7) and 171.97(9°)). In both cases, the sum of the bond angles around the oxygen atom in the PNP ligand is 360°, which indicates the delocalization of the nitrogen lone pair through phosphorous atoms by adopting sp²-hybridization. The sum of the bond angles around the oxygen atom in THF is 360°, indicating π-donation from the O to the CrIII center by adopting sp²-hybridization. The Cr−O−THF distances are elongated in \( \text{[1-CrCl}_2(\text{THF})_2\text{]}^+\text{[B(C_F_5)_4]}^- \) when compared to those in \( \text{[(THF)_4CrCl}_2\text{]}^+\text{[B(C_F_5)_4]}^- \) (average 2.042 vs 2.003 Å).

Ethylene Tetramerization Studies. As shown in Table 1, the \( \text{[(PNP)CrCl}_2$(\text{CH}_3\text{CN})_2\text{]}^+\text{[B(C_F_3)_4]}^- \) complexes were screened for ethylene oligomerization after activation with trialkylaluminum agents (Me₃Al, Et₃Al, or iBu₃Al) with the expectation that the trialkylaluminum would replace the chloride ligands with alkyl groups (i.e., Me, Et, or iBu) and abstract the acetonitrile ligands to generate vacant sites for ethylene coordination, thus generating the active species necessary for the catalytic cycle involving cationic CrIII species. As expected, the \( \text{[1-CrCl}_2$(\text{CH}_3\text{CN})_2\text{]}^+\text{[B(C_F_3)_4]}^- / \text{Me}_3\text{Al} (\text{Al/Cr}, 300) \) catalytic system shows high activity (155 kg g⁻¹Cr⁻¹h⁻¹) in chlorobenzene, in which \( \text{[(THF)_4CrCl}_2\text{]}^+\text{[B(C_F_5)_4]}^- \) is soluble, with reasonable selectivity (1-hexene 42%, 1-octene 44%, PE 2.2%; entry 1). As anticipated, the catalytic system based on the bis(PNP)Cr complex, that is, \( \text{[1,2-CrCl}_2$(\text{CH}_3\text{CN})_2\text{]}^+\text{[B(C_F_3)_4]}^- / \text{Me}_3\text{Al} \) shows low activity (50 kg g⁻¹Cr⁻¹h⁻¹, entry 2). The use of Me₃Al is not preferable to the use of MAO because the price of MAO is elevated mainly by the high cost of Me₃Al. The use of Et₃Al or iBu₃Al instead of Me₃Al lowers the activity (74 and 126 kg g⁻¹Cr⁻¹h⁻¹, respectively) and resulted in the formation of a significant amount of PE (ca. 10%, entries 3 and 4). We attributed these unsatisfactory results to incomplete alkylation, owing to the lower reactivity of Et₃Al and iBu₃Al compared to that of Me₃Al. When a small proportion of Me₃Al (30 μmol, Al/Cr = 20) is admixed with Et₃Al (420 μmol), the activity becomes even higher (288 kg g⁻¹Cr⁻¹h⁻¹) than that observed for \( \text{[1-CrCl}_2$(\text{CH}_3\text{CN})_2\text{]}^+\text{[B(C_F_3)_4]}^- / \text{Me}_3\text{Al} \) (entry 5). The selectivity of this improved system is also satisfactory, with formation of only a negligible amount of PE (0.7%). Similar improvement is also achieved avoiding the use of any Me₃Al using Et₃Al or iBu₃Al alone and allowing 1 h activation time. Thus, the activities (224 and 221 kg g⁻¹Cr⁻¹h⁻¹, entries 6 and 7) become comparable to those of the system containing MAO, that is, \( \text{[1-CrCl}_2\text{]}^+\text{[B(C_F_3)_4]}^- / \text{Et}_3\text{Al} \) (entry 8) when \( \text{[1-CrCl}_2$(\text{CH}_3\text{CN})_2\text{]}^+\text{[B(C_F_3)_4]}^- \) is used after activation with Et₃Al or iBu₃Al for 1 h. The selectivity is also similar to that observed with \( \text{[1-CrCl}_2\text{]}^+\text{[B(C_F_3)_4]}^- / \text{MAO} \), generating only a small amount of PE (1%).

Aliphatic hydrocarbon solvents, for example, methycyclohexane, are reported to be the best choice for the ethylene oligomerization reaction considering their boiling point and safety. Upon changing the solvent from chlorobenzene to methycyclohexane, in which \( \text{[1-CrCl}_2$(\text{CH}_3\text{CN})_2\text{]}^+\text{[B(C_F_3)_4]}^- \) is insoluble, the activity of \( \text{[1-CrCl}_2$(\text{CH}_3\text{CN})_2\text{]}^+\text{[B(C_F_3)_4]}^- / \text{Et}_3\text{Al} \) (or iBu₃Al) becomes unsatisfactorily low (13 and 26 kg g⁻¹Cr⁻¹h⁻¹, entries 10 and 11). However, \( \text{[2-CrCl}_2$(\text{CH}_3\text{CN})_2\text{]}^+\text{[B(C_F_3)_4]}^- / \text{Et}_3\text{Al} \) (77 and 84 kg g⁻¹Cr⁻¹h⁻¹, entries 12 and 13). The activity achieved is ca. 50% that is attained with the original MAO-based Sasol system (1/Cr(acac)₃/MAO) under otherwise identical conditions (163 kg g⁻¹Cr⁻¹h⁻¹, entry 16). Furthermore, the performance of this catalytic system exhibits negligible deactivation over the rather long reaction time of 1.5 h; the ethylene consumption and hence the productivity increase almost linearly with time and reach 134 kg g⁻¹Cr⁻¹h⁻¹ by running the oligomerization for 1.5 h (entry 14, Figure 3a). Another advantage of this system is that unwanted side products above C₁₀ labeled as ">C₁₀" labeled in Table 1 were lowered (ca. 9 vs 13%) by the use of \( \text{[2-CrCl}_2$(\text{CH}_3\text{CN})_2\text{]}^+\text{[B(C_F_3)_4]}^- / \text{Et}_3\text{Al} \) (or iBu₃Al) instead of 1/Cr(acac)₃/MAO, even though the 1-hexene/1-octene ratio becomes higher (14/70 vs 8/73). Coproduction of 1-hexene and 1-octene is an acceptable option in industry, and the higher 1-hexene/1-octene ratio is not a critical disadvantage. Another type of cationic Cr complex paired with the \( \text{[B(C_F_3)_4]}^- \) anion, \( \text{[2-CrCl}_2$(\text{CH}_3\text{CN})_2\text{]}^+\text{[B(C_F_3)_4]}^- / \text{Et}_3\text{Al} \) (or iBu₃Al) almost doubles by changing the methycyclohexane solvent to cyclohexene. A similar trend was also observed in the original MAO-based Sasol system; the activity drops by half upon changing the methycyclohexane solvent to cyclohexene. A similar trend was also observed in the original MAO-based Sasol system; the activity drops by half upon changing the methycyclohexane solvent to cyclohexene.

Figure 3. Ethylene consumption vs time monitored by a mass-flow controller (MFC) in the tetramerization reaction performed in methycyclohexane (a) or cyclohexene (b) using \( \text{[2-CrCl}_2$(\text{CH}_3\text{CN})_2\text{]}^+\text{[B(C_F_3)_4]}^- / \text{Et}_3\text{Al} \) or \( \text{Et}_3\text{Al} \).

Table 1. Catalytic Activity of Various Cr Complexes in Ethylene Tetramerization.
MAO) in methylcyclohexane (168 vs 163 kg/g-Cr/h). The same high activity is attained when activator iBu3Al is replaced with the more common and cheaper Et3Al (entry 19) and, moreover, the catalyst deactivation is negligible over the course of 1 h oligomerization (entry 20, Figure 3b). The π bond in cyclohexene does not participate in product formation; no additional signals are observed in the gas chromatography (GC) chart with the use of cyclohexene instead of methylcyclohexane (Figures S2 and S3). The formation of slightly fewer unwanted side products >C10 (5.3–8.0%) and formation of negligible amounts of PE (0.1–0.3%) are other advantages observed for the use of cyclohexene. Cyclohexene is an inexpensive and abundant chemical currently used in industry on a large scale, and its boiling point is di

The activities of [2-CrCl3(CH3CN)2][B(C6F5)4]/EtAl (or iBu3Al) achieved in this work (89 and 168 kg/g-Cr/h in methylcyclohexane and cyclohexene, respectively) are significantly higher than that previously reported for 1

Cationic (PNP)CrIII complexes paired with [B(C6F5)4]− anion ([PNP]CrCl3(CH3CN)2][B(C6F5)4]−, where PNP is PPN-(PPh2)2 (1) or [(PNP)CrCl3(CH3CN)2][B(C6F5)4]−, activated with EtAl or iBu3Al, showed high activity in ethyl-

EXPERIMENTAL SECTION

CONCLUSIONS

Figure 4. 19F NMR spectra of [(CH3CN)4CrCl2][B(C6F5)4]− (a), [1-CrCl3(CH3CN)2][B(C6F5)4]− (b), [1-CrCl3(CH3CN)2][B-(C6F5)4]−/iBuAl (Al/Cr, 20) (c), and [Li][B(C6F5)4]−/iBuAl (Al/Li, 20) (d).

-164 to −167 (meta) ppm (Figure 4a,b). In the 19F NMR spectrum of [1-CrCl3(CH3CN)2][B(C6F5)4]−/iBuAl (Al/Cr, 20) in chlorobenzene-d5, only the ortho-signal at −133 ppm is observed (Figure 4c); the signals for the para- and meta-fluorine are absent, possibly due to interaction with the paramagnetic CrIII center. The stability of the [B(C6F5)4]− anion itself in the presence of iBu3Al is further indicated by the close presence of a set of −CF3 signals alone at −134, −157, and −162 ppm for [Li][B(C6F5)4]−/iBuAl (Al/Li, 20) in chlorobenzene-d5 (Figure 4d). In this study, [Ph3C][B-(C6F5)4]− is not used with the trialkylaluminum reagent, but cationic CrIII complexes paired with [B(C6F5)4]− anions were prepared by an alternative route. By avoiding the use of [Ph3C][B(C6F5)4]−, an efficient catalytic system containing [B(C6F5)4]− anions may be realized.

■ CONCLUSIONS

The activities of [2-CrCl3(CH3CN)2][B(C6F5)4]−/EtAl (or iBu3Al) achieved in this work (89 and 168 kg/g-Cr/h in methylcyclohexane and cyclohexene, respectively) are significantly higher than that previously reported for 1

The activities of [2-CrCl3(CH3CN)2][B(C6F5)4]−/EtAl (2.5 kg/g-Cr/h).42 The low activity in the latter case was attributed to the destruction of [B(C6F5)4]− anions by the action of Et3Al; [Ph3C][B(C6F5)4]− was reported to react with trialkylaluminum, with the [B(C6F5)4]− anion being fragmented. We believe that this instability is triggered by the reaction of the trialkylaluminum reagent with the trityl cation ([Ph3C]+), not by the reaction with the [B(C6F5)4]− anion itself.42 The 19F NMR signals were monitored to investigate the stability of the [B(C6F5)4]− anion (Figure 4). In the 19F NMR spectra of [(CH3CN)4CrCl2][B(C6F5)4]− (a), [1-CrCl3(CH3CN)2][B(C6F5)4]− (b), [1-CrCl3(CH3CN)2][B-(C6F5)4]−/iBuAl (Al/Cr, 20) (c), and [Li][B(C6F5)4]−/iBuAl (Al/Li, 20) (d).

■ EXPERIMENTAL SECTION

General Remarks. All manipulations were performed under an inert atmosphere using a standard glove box and Schlenk techniques. Methylene chloride, acetonitrile, chlorobenzene, and Cd2Cl2 were stirred over CaH2 and transferred to the reservoir under vacuum. Toluene, hexane, THF, and CdD2 were distilled from benzophenone ketyl. Methylcyclohexane (anhydrous grade), toluene, and cyclohexene used for the oligomerization reactions were 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 40 bar pressure. The 1H NMR (400 MHz), 13C NMR (100 MHz), and 31P NMR (162 MHz) spectra were recorded on a Varian
Mercury plus 400 spectrometer. Elemental analyses were carried out at the Analytical Center, Ajou University. GC-flame ionization detection (GC-FID) analysis was performed on an YL instrument 6500GC system equipped with a HP-PONA (50 m × 0.200 mm × 0.50 μm) column. CrCl(THF)₄ₕ孵 [Ag(CH₃CN)₄]⁺[B(C₆F₅)₄]⁻, 58 [H-(OEt₂)]⁻[B(C₆F₅)₄]⁻, 59 and 18-aminopentriacontane ([CH₃(CH₂)₁₈]₂CHNH₂) were prepared by literature methods. Modified MMAO-3A was sourced from Akzo Nobel (7.0 Al wt % in heptane).

\[
\{\text{L} \text{CrCl}_{2}\}^{+}[\text{B}(\text{C}_6\text{F}_5)_{4}]^{-} (\text{L} = \text{CH}_3\text{CN}, \text{THF})
\]

A solution of Ag(CH₃CN)₄[B(C₆F₅)₄] (2.54 g, 2.67 mmol) in acetonitrile (15 mL) was added to a solution of CrCl₂(THF)₄ (1.00 g, 2.67 mmol) in acetonitrile (15 mL). AgCl immediately precipitated as gray solids. After stirring overnight, the precipitates were removed by filtration. The filtrate was concentrated in vacuo to give a residue that was redissolved in acetonitrile (ca. 4 mL). Green thin needle-shaped microcrystals were deposited when the solution was kept at a freezer at −30 °C. The deposited green microcrystals were isolated by decantation (1.55 g, 60%). Anal. Calcd for [(CH₃ CN)₄ CrCl₂]⁺[B(C₆F₅)₄]⁻: C, 56.54; H, 3.29; N, 2.39%. Found: C, 59.69; H, 6.06; N, 1.94%.

\[
[1-\text{CrCl}_2(\text{CH}_3\text{CN})_2]^+ [\text{B}(\text{C}_6\text{F}_5)_{4}]^{-} (1 = \text{iPrN(PPh}_2)_2)
\]

A solution of iPrN(PPh₂)₂ (0.089 g, 0.21 mmol) in methylene chloride (0.5 mL) was added dropwise to a solution of [(CH₃CN)₂CrCl₂]⁺[B(C₆F₅)₄]⁻ (0.200 g, 0.207 mmol) in methylene chloride (1.5 mL). Upon addition, the color of the solution changed immediately from olive green to brown and finally became bluish-green after 3 h. The solvent was removed under vacuum to obtain an oily residue, which was redissolved in methylene chloride (3 mL). The resulting solution was stirred overnight. After filtration, the volatiles in the filtrate were removed under vacuum. The residue was dissolved in methylene chloride (3 mL) and insoluble impurities were removed by filtration. The solution was concentrated in vacuo to obtain a red solid (0.147 g, 73%). Anal. Calcd for [(CH₃(CH₂)₁₈]₂CHNH₂ (0.505 g, 0.994 mmol) in methylene chloride (5 mL) was added dropwise at 0 °C to a solution of Ph₃P (0.082 g, 0.185 mmol) in methylene chloride (3 mL). Upon addition, the color of the solution changed immediately from olive green to bluish-green and finally became green after 3 h. The solvent was removed under vacuum. The residue was redissolved in methylene chloride (3 mL) and all volatiles were completely removed to obtain a bluish-green residue. Methylcyclohexane (10 mL) was added and the product was dissolved by heating to ca. 50 °C using a heat gun. The solution was filtered through Celite while it was hot. The solvent was then removed under vacuum, and the residue was redissolved in hot methylcyclohexane (10 mL). The solution was again filtered through Celite at ca. 50 °C to remove any insoluble impurities. Removing the solvent under vacuum afforded a greenish waxy solid (0.147 g, 73%). Anal. Calcd for C₃₅H₃₅BCl₂CrF₄N₄P₂ (1760.38 g mol⁻¹): C, 59.36; H, 5.55; N, 2.39%. Found: C, 59.69; H, 6.06; N, 1.94%.

\[
[\text{o-Me} \text{NC}(\text{C}_6\text{H}_5)_2] \text{CrCl}_2
\]

n-BuLi (2.5 M in hexane, 10.3 g, 37.2 mmol) was added to a solution of N,N-dimethyl-1,3,4-oxadiazine (5.00 g, 37.0 mmol) in a mixture of hexane (20 mL) and diethyl ether (10 mL). After stirring overnight at 45 °C, the generated solids were isolated by filtration. The isolated pale yellow solid (2-dimethylaminobenzylithium, 4.23 g, 30.0 mmol, 81%) was dissolved in THF (30 mL), and the resulting solution was added to a stirred suspension of CrCl₂(THF)₃ (3.74 g, 9.98 mmol) in THF (30 mL) at −78 °C. Upon stirring at −78 °C for 1 h, the color of the solution changed from bright purple to dark orange. The reaction mixture was then warmed to room temperature and stirred overnight. The color of the solution changed from dark orange to dark red. The solvent was removed under vacuum to obtain the solids that were washed with diethyl ether (60 mL). Methylene chloride (100 mL) was added to dissolve the product, and insoluble byproducts were removed by filtration. The solvent was removed under vacuum to obtain a red solid (3.31 g, 73%). The product was further purified by recrystallization from methylene chloride at −30 °C.
[2-Cr(CH2C6H4NMe2)2][B(C6F5)4]−. A solution of [H-(OEt2)2]−[B(C6F5)4]− (0.183 g, 0.221 mmol) in methylene chloride (0.5 mL) was added dropwise to a solution of (o-Me3NC6H4CH2)2Cr (0.100 g, 0.220 mmol) in methylene chloride (3 mL). Upon addition, the color of the solution changed immediately from dark red to violet. After stirring for 1 h, a solution of [CH3(CH2)16CHN(PPh2)2] (0.193 g, 0.220 mmol) in methylene chloride (2 mL) was added dropwise. Upon addition, the color of the solution changed immediately from violet to dark orange and became green after stirring overnight. All volatiles were removed under vacuum. Methylcyclohexane (10 mL) was added, and the product was dissolved by heating to 50 °C with a heat gun. The solution was filtered through Celite while hot. Removing the solvent under vacuum afforded a greenish waxy solid (0.280 g, 68%), which was used for the oligomerization studies without further purification and characterization.

**Typical Procedure for Ethylene Oligomerization**

(Entry 19 in Table 1). In a glove box, a dried 75 mL bomb reactor was charged with cyclohexene (19 mL) and Et3Al (0.450 mmol). The reactor was assembled and removed from the glove box. The reactor was then heated to 35 °C using an oil bath. The chromium complex (1.5 μmol) dissolved in cyclohexene (1 mL) was injected into the reactor using a syringe. Ethylene gas (45 bar) was immediately fed into the reactor. The temperature immediately increased to 45 °C owing to the generated heat. Ethylene consumption was monitored using a MFC under a constant pressure of 45 bar. After conducting the oligomerization at 45 °C for 30 min, the reactor was cooled with an ice bath and the ethylene gas was vented off. Ethanol (2 mL), aqueous HCl (10%, 2 mL), and water (3 mL). Upon addition, the color of the solution changed immediately from dark red to violet. After stirring for 1 h, the reaction mixture was filtered through Celite, and the organic upper layer was taken for GC analysis. The organic upper layer was then concentrated in vacuo. The resulting waxy product was purified by column chromatography on silica gel (CH2Cl2/Methanol = 20/1) to afford a greenish waxy solid (0.280 g, 68%), which was used for the oligomerization studies without further purification and characterization.

**Crystallographic Data**

Crystallographic data for [(CH3CN)4Ag]+[B(C6F5)4]− are available in the Supporting Information (CCDC #, 1515444; Supporting Information): C27H36CrN3, M = 545.59, monoclinic, a = 7.0261(3), b = 28.8953(11), c = 11.9390(5) Å, β = 100.211(2)°, V = 2385.48(17) Å3, T = 100(2) K, space group P21/n, Z = 4, 4055 unique (R(int) = 0.0150), which were used in all calculations. The final ωR2 was 0.0923 (I > 2σ(I)).

Crystallographic data for [1-CrCl2(THF)2][B(C6F5)4]− (CCDC #, 1515445; Supporting Information): C78H55BCrCl2Fe2NO3P2, M = 1699.59, monoclinic, a = 20.9402(14), b = 17.8800(12), c = 17.0227(12) Å, β = 113.683(4)°, V = 5836.7(7) Å3, T = 100(2) K, space group P21/c, Z = 4, 10574 unique (R(int) = 0.1041), which were used in all calculations. The final ωR2 was 0.1433 (I > 2σ(I)).

Crystallographic data for [1-CrCl2][B(C6F5)4]− (CCDC #, 1515446; Supporting Information): C26H15ClCrF2O2N2P2, M = 1699.59, monoclinic, a = 20.9402(14), b = 17.8800(12), c = 17.0227(12) Å, β = 113.683(4)°, V = 5836.7(7) Å3, T = 100(2) K, space group P21/c, Z = 4, 10574 unique (R(int) = 0.1041), which were used in all calculations. The final ωR2 was 0.1433 (I > 2σ(I)).

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