





## Article

# Replacement of the Common Chromium Source $\text{CrCl}_3(\text{thf})_3$ with Well-Defined $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$

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**Abstract:**  $\text{CrCl}_3(\text{thf})_3$  is a common starting material in the synthesis of organometallic and coordination compounds of Cr. Deposited as an irregular solid with no possibility of recrystallization, it is not a purity guaranteed chemical, causing problems in some cases. In this work, we disclose a well-defined form of the THF adduct of  $\text{CrCl}_3$  ( $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$ ), a crystalline solid, that enables structure determination by X-ray crystallography. The EA data and XRD pattern of the bulk agreed with the revealed structure. Moreover, its preparation procedure is facile: evacuation of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  at 100 °C, treatment with 6 equivalents of  $\text{Me}_3\text{SiCl}$  in a minimal amount of THF, and crystallization from  $\text{CH}_2\text{Cl}_2$ . The ethylene tetramerization catalyst  $[\text{iPrN}\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-Si}(\text{nBu})_3)_2\}_2\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  prepared using well-defined  $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$  as a starting material exhibited a reliably high activity (6600 kg/g-Cr/h; 1-octene selectivity at 40 °C, 75%), while that of the one prepared using the impure  $\text{CrCl}_3(\text{thf})_3$  was inconsistent and relatively low (~3000 kg/g-Cr/h). By using well-defined  $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$  as a Cr source, single crystals of  $[(\text{CH}_3\text{CN})_4\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  and  $[\text{Et}(\text{Cl})\text{Al}(\text{N}(\text{iPr})_2)_2\text{Cr}(\mu\text{-Cl})_2]$  were obtained, allowing structure determination by X-ray crystallography, which had been unsuccessful when the previously known  $\text{CrCl}_3(\text{thf})_3$  was used as the Cr source.

**Keywords:** chromium compound;  $\text{CrCl}_3(\text{thf})_3$ ;  $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$ ; ethylene tetramerization catalyst



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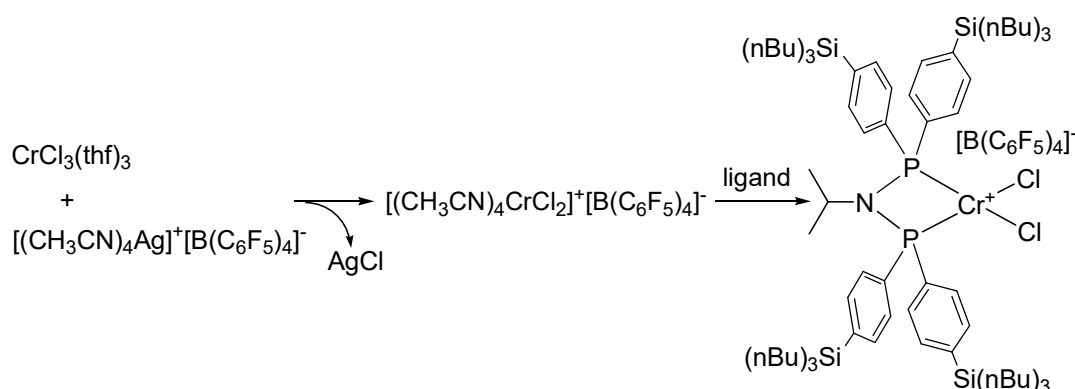


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## 1. Introduction

$\text{CrCl}_3(\text{thf})_3$  has been widely used as a starting material for the synthesis of organometallic and coordination compounds of Cr [1–10]. Its preparation method was reported 60 years ago; anhydrous  $\text{CrCl}_3$ , which is insoluble in organic solvents as well as in water, was extracted with THF by the aid of Zn dust using Soxhlet apparatus [11–13]. However, anhydrous  $\text{CrCl}_3$  is prepared by hazardous and not-facile process (treatment of  $\text{Cr}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  with  $\text{CCl}_4$  at 630 °C leads to the generation of extremely toxic phosgene gas), and thus, is expensive [14,15]. Another method was reported in which  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  was reacted with excess thionyl chloride ( $\text{S}(\text{O})\text{Cl}_2$ ) to generate anhydrous  $\text{CrCl}_3$ . In this process, a different form of hygroscopic  $\text{CrCl}_3$  was generated, from which  $\text{CrCl}_3(\text{thf})_3$  could be immediately obtained after adding THF [16–18]. The most attractive and convenient method is reacting  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  with excess  $\text{Me}_3\text{SiCl}$  in THF, resulting in the deposition of  $\text{CrCl}_3(\text{thf})_3$  along with the generation of byproducts, HCl and  $\text{Me}_3\text{SiOSiMe}_3$  ( $\text{CrCl}_3 \cdot 6\text{H}_2\text{O} + 12 \text{Me}_3\text{SiCl} \rightarrow \text{CrCl}_3(\text{thf})_3 + 12 \text{HCl} + 6 \text{Me}_3\text{SiOSiMe}_3$ ) [19]. Excess  $\text{Me}_3\text{SiCl}$  (~60 equiv./Cr) needs to be added to obtain a completely anhydrous form of  $\text{CrCl}_3(\text{thf})_3$  [20]. Otherwise (e.g., when 25 equiv. of  $\text{Me}_3\text{SiCl}/\text{Cr}$  was added according to the literature), hydrated  $\text{CrCl}_3(\text{thf})_2(\text{H}_2\text{O})$  is obtained, which was erroneously sold as  $\text{CrCl}_3(\text{thf})_3$  in the past [20,21].

Sasol disclosed a catalyst system composed of a Cr source,  $iPrN(PPh_2)_2$  ligand, and methylaluminoxane (MAO), which produces mainly 1-octene through ethylene tetramerization [22–24].  $CrCl_3(thf)_3$  has been actively used as a component of the ethylene tetramerization catalyst system [25–34]. We also developed a very efficient catalyst for ethylene tetramerization (Scheme 1) [35–37]. The catalyst shows extremely high activity ( $\sim 5000$  kg/g-Cr/h) and is advantageous over other reported systems in that it works with an inexpensive activator,  $iBu_3Al$ , avoiding the use of expensive MAO in excess ( $Al/Cr = 300\text{--}500$ ) [38–43]. During the course of the studies, we had a problem in reproducing such an extremely high activity and eventually found that the Cr source  $CrCl_3(thf)_3$  used in the preparation was the cause of this problem. Although the structure of  $CrCl_3(thf)_3$  was revealed by X-ray crystallography, using a single crystal selected from the batch in the Soxhlet extraction process, it does not redeposit as good-quality crystals when redissolved in  $CH_2Cl_2$  [44,45]. Structure elucidated by X-ray crystallography does not guarantee the purity of the bulk and we questioned the purity of the common Cr source  $CrCl_3(thf)_3$ . In fact, it was reported as an “irregular violet solid” which may mean that it is not a pure  $CrCl_3(thf)_3$  but a mixture containing other forms of THF adduct of  $CrCl_3$  (e.g.,  $\mu_2$ -Cl bridged multinuclear species) [46]. Elemental analysis (EA) data for Cr and Cl have been reported, but common carbon and hydrogen data were missing.  $CrCl_3(thf)_3$  is paramagnetic; thus, it cannot be subjected to structural analysis using  $^1H$  and  $^{13}C$  NMR spectroscopy. We also previously found that the composition (as well as the structure) of the commercial source of  $(2\text{-ethylhexanoate})_3Cr$ , another type of important paramagnetic Cr(III) complex that is commercially used as a component in the Phillips ethylene trimerization catalyst [47], is erroneous [21,48]. By correcting the structure to  $(2\text{-ethylhexanoate})_2CrOH$ , the catalytic performance was consistent and, moreover, significantly improved.



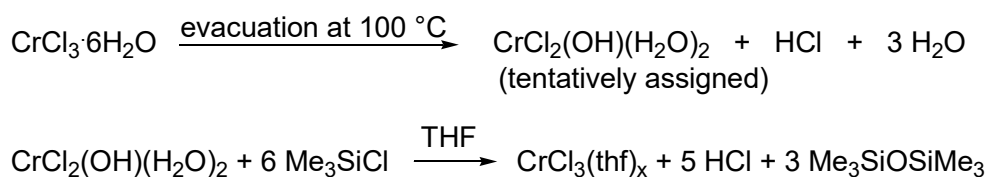
**Scheme 1.** Preparation of extremely active ethylene tetramerization catalyst.

## 2. Results and Discussion

$CrCl_3(thf)_3$  was commercially available from Aldrich (St. Louis, MO, USA), but we prepared it to ensure complete dryness by reacting  $CrCl_3 \cdot 6H_2O$  with excess  $Me_3SiCl$  (60 equiv.) [20]. We modified the procedure as follows:  $CrCl_3 \cdot 6H_2O$  was evacuated for  $\sim 6$  h before the treatment with  $Me_3SiCl$ . The catalyst  $[iPrN\{P(C_6H_4\text{-}p\text{-}Si(nBu)_3)_2\}_2CrCl_2]^+[B(C_6F_5)_4]^-$ , prepared according to Scheme 1 using  $CrCl_3(thf)_3$ , which was prepared via the evacuation step, provided extremely high activity ( $\sim 5000$  kg/g-Cr/h). In contrast, the catalyst prepared using either the commercial source of  $CrCl_3(thf)_3$  or the one prepared according to the reported method without the evacuation step did not exhibit such a high activity ( $\sim 3000$  kg/g-Cr/h), and there was some amount of methylcyclohexane-insoluble fraction when ligand  $iPrN\{P(C_6H_4\text{-}p\text{-}Si(nBu)_3)_2\}_2$  was reacted with  $[(CH_3CN)_4CrCl_2]^+[B(C_6F_5)_4]^-$ . The insoluble fraction was negligible when  $CrCl_3(thf)_3$ , which was prepared via the evacuation step, was used as the starting material.

We investigated what happened in the evacuation step. When the crystalline form of  $CrCl_3 \cdot 6H_2O$  (10 g, 37.5 mmol) was evacuated at  $100^\circ C$ , the color gradually changed

from dark green to light green, light gray, and finally light purple with gradual loss of weight. Finally, an amorphous powder was obtained, and the weight loss converged to 36% (6.39 g remaining). Further weight reduction was minimal when the evacuation time was increased. It was confirmed with litmus paper that the removed volatile component was not pure water but acidic, presumably containing HCl. From these observations, the remaining Cr compound was tentatively considered as  $\text{CrCl}_2(\text{OH})(\text{H}_2\text{O})_2$ ; 34% weight loss is expected for the transformation of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  to  $\text{CrCl}_2(\text{OH})(\text{H}_2\text{O})_2$  (Scheme 2). The structure of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  was reported to be  $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ , and the action of heat under vacuum could liberate outer-sphere  $\text{Cl}^-$  (as HCl with a proton in an inner-sphere water) and three water molecules (two from the outer sphere and one from the inner sphere), consequently leaving  $\text{CrCl}_2(\text{OH})(\text{H}_2\text{O})_2$  (possibly,  $[\text{CrCl}_2(\text{H}_2\text{O})_2(\mu\text{-OH})]_2$  adopting an octahedral structure) in the reaction pot.

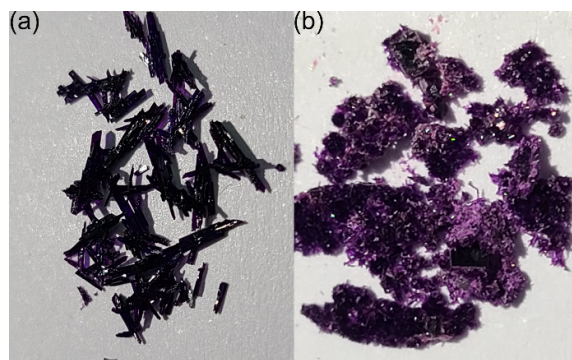


**Scheme 2.** Modified preparation method for THF adduct of  $\text{CrCl}_3$ .

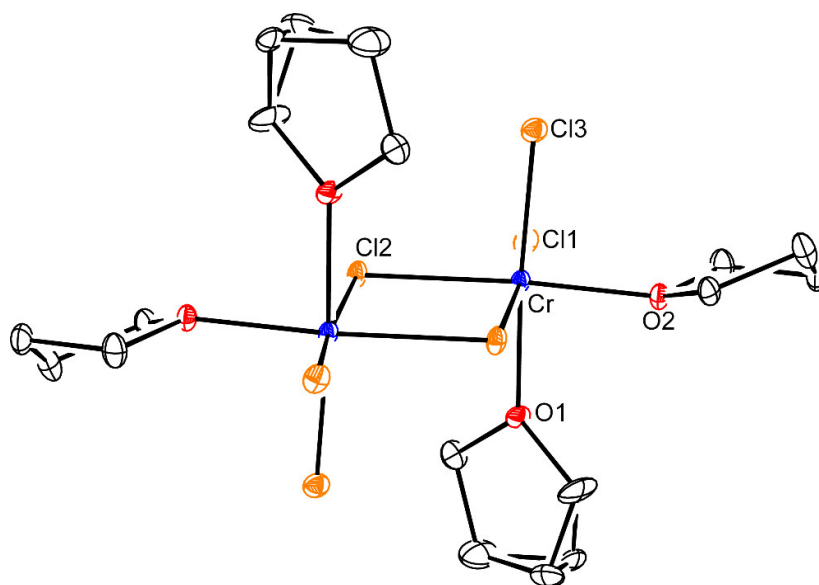
Treatment of  $\text{CrCl}_2(\text{OH})(\text{H}_2\text{O})_2$ , after dissolving in THF, with  $\text{Me}_3\text{SiCl}$  resulted in the precipitation of a violet solid, which was confirmed by infrared spectroscopy to be completely anhydrous. Because a large portion of  $\text{H}_2\text{O}$  in  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  was removed at the evacuation step, 6.0 equiv.  $\text{Me}_3\text{SiCl}$  (equivalent amount that needed for the transformation of  $\text{CrCl}_2(\text{OH})(\text{H}_2\text{O})_2$  to  $\text{CrCl}_3(\text{thf})_x$ , Scheme 2) was added instead of 60 equiv./Cr, and accordingly, the amount of THF could be minimized (36 mL/10 g— $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ). The color and shape of the precipitated solid (irregular violet solid) were almost identical to that of the commercial source of  $\text{CrCl}_3(\text{thf})_3$  and the one prepared without the evacuation step. However, as aforementioned, the catalyst performance was significantly better when using  $\text{CrCl}_3(\text{thf})_3$  prepared via the evacuation step. The product of the reaction between  $[(\text{CH}_3\text{CN})_4\text{Ag}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  and  $\text{CrCl}_3(\text{thf})_3$  (i.e.,  $[(\text{CH}_3\text{CN})_4\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ) differed depending on the source of  $\text{CrCl}_3(\text{thf})_3$ . Although  $[(\text{CH}_3\text{CN})_4\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  was isolated by precipitation in  $\text{CH}_3\text{CN}$  at  $-30\text{ }^\circ\text{C}$ , the precipitate was not composed of good-quality crystals; thus, X-ray crystallography could not be used for characterization. We crosschecked the tentatively assigned structure of  $[(\text{CH}_3\text{CN})_4\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  by counting the number of  $\text{CH}_3\text{CN}$  molecules per each Cr atom through the analysis of integration values in the  $^1\text{H-NMR}$  spectra recorded using  $\text{THF-d}_8$  with 9-methylanthracene as an internal standard. For the product obtained using  $\text{CrCl}_3(\text{thf})_3$  prepared via the evacuation step, the number of  $\text{CH}_3\text{CN}$  per Cr was in good agreement with the expected value of 4 (4.1, 3.8, or 4.0). In contrast, the number deviated from 4 (6.5, 6.1, 5.3, or 6.2) when either the commercial source of  $\text{CrCl}_3(\text{thf})_3$  or the one prepared without the evacuation step was used.

The most striking difference between the two samples was that good-quality crystals were deposited in a  $\text{CH}_2\text{Cl}_2$  solution of  $\text{CrCl}_3(\text{thf})_3$  that was prepared via the evacuation step, whereas an irregular solid was deposited when either the commercial source of  $\text{CrCl}_3(\text{thf})_3$  or the one prepared without the evacuation step was dissolved in  $\text{CH}_2\text{Cl}_2$  (Figure 1). X-ray crystallography studies revealed that the deposited crystals were a Cl-bridged dinuclear complex  $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$  (Figure 2). The Cr atom adopted an octahedral structure, with two THFs being in the cis-position. The bond distances between Cr and terminal-Cl (2.277 and 2.289 Å) were shorter than that between Cr and bridge-Cl (2.362 Å) as well as the Cr–Cl distances (3.299, 3.318, and 3.352 Å) observed for *mer*- $\text{CrCl}_3(\text{thf})_3$ , whose structure has been previously revealed using a single crystal obtained from the reaction pot of  $\text{Cr}(\text{CH}_2\text{SiMe}_3)_4$  and HCl in THF (CCDC# 983659) [20]. The distance between Cr and  $\text{O}^{\text{THF}}$  situated trans to terminal-Cl was greater than that between Cr and

$O^{THF}$  situated trans to bridge-Cl (2.045 vs. 2.018 Å). The  $O^{THF}$  atom situated trans to terminal-Cl adopted perfect trigonal planar geometry (sum of bond angle around O1 atom,  $360.0^\circ$ ), indicating  $\pi$ -donation from O to Cr through adopting  $sp^2$ -hybridization. The other  $O^{THF}$  atom situated trans to bridge-Cl deviated from a perfect trigonal planar geometry (sum of bond angle around O1 atom,  $352.8^\circ$ ).



**Figure 1.** Macroscopic views of crystals of  $[CrCl_2(\mu-Cl)(thf)_2]_2$  (a) and irregular solid known as  $CrCl_3(thf)_3$  (b).

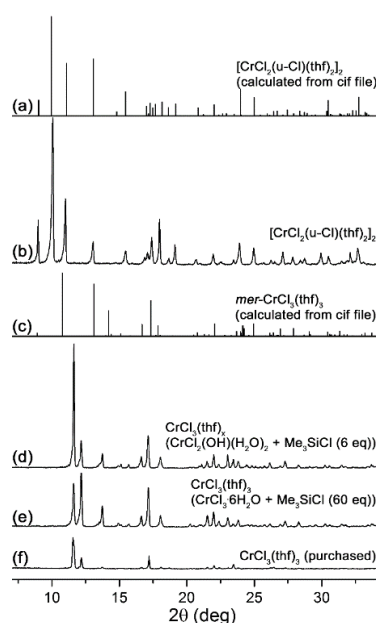


**Figure 2.** X-ray structure of  $[CrCl_2(\mu-Cl)(thf)_2]_2$ . Selected bond distances (Å) and angles ( $^\circ$ ): Cr-Cl1, 2.2773(12); Cr-Cl2, 2.3622(12); Cr-Cl3, 2.2885(11); Cr-O1, 2.045(3); Cr-O2, 2.018(3); C-O1-C,  $109.5(3)$ ; C-O1-Cr,  $125.5(2)$ ; C-O1-Cr,  $125.0(2)$ ; C-O2-C,  $108.7(3)$ ; C-O2-Cr,  $121.5(2)$ ; and C-O2-Cr,  $122.6(2)$ .

X-ray crystallography data do not guarantee the purity of the bulk. The EA data of C were roughly in agreement with the values calculated for the revealed structure  $[CrCl_2(\mu-Cl)(thf)_2]_2$  (31.8%), although the measured values were not always within the required range of  $31.8\% \pm 0.4\%$  (30.7%, 30.9%, 30.4%, 31.0%, 30.5%, 30.2%, 30.4%, 30.9%, and 31.2%). In contrast, the EA data of C measured for either the commercial source of  $CrCl_3(thf)_3$  or the one prepared without the evacuation step deviated substantially from the value calculated for  $CrCl_3(thf)_3$  (38.5%). The data fluctuated severely by variation in sampling points (32.4%, 26.5%, 34.1%, 38.1%, and 33.8% for a bottle of purchased sample; 34.2%, 36.7%, 37.1%, 35.3%, and 34.1% for another bottle of purchased sample; 31.3%, 30.5%, 37.0%, 33.6%, and 33.9% for the sample prepared without the evacuation step). Before recrystallization, the sample prepared via the evacuation step also showed fluctuating C content by varying the sampling point, and the C content agreed neither with the structure of  $CrCl_3(thf)_3$  nor

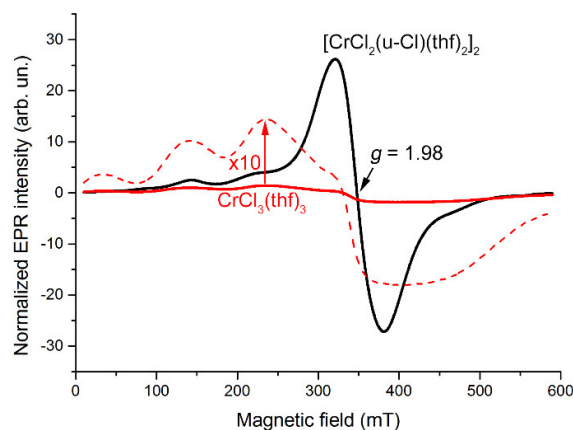
the structure of  $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$  (35.3%, 34.3%, 32.5%, 34.2%, and 32.4%). Though the carbon contents and the XRD pattern are inconsistent with the formula of the commercial source  $\text{CrCl}_3(\text{THF})_3$ , the Cr content measured by ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy) and the Cl content measured by gravimetric analysis after treatment of  $\text{AgNO}_3$  to aqueous solution of  $\text{CrCl}_3(\text{THF})_3$  were not severely deviated from the values calculated for the formula  $\text{CrCl}_3(\text{THF})_3$  (Calcd. Cr 13.88, Cl 28.38. Found: Cr 14.04, Cl 29.09%). The Cr content measured for the prepared  $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$  agreed accurately with the calculated value while the measured Cl content was slightly deviated (Calcd. Cr 17.19, Cl 35.15. Found: Cr 17.18, Cl 34.58%).

The X-ray powder diffraction (XRD) pattern observed for bulk  $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$  isolated via the recrystallization procedure agreed well with single-crystal X-ray crystallography data (cif file) (Figure 3a vs. Figure 3b), indicating that the majority of deposited solid had a structure of  $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$ . In contrast, the XRD pattern of the purchased  $\text{CrCl}_3(\text{thf})_3$  or the one prepared by the reported method without the evacuation step did not agree with single-crystal X-ray crystallography data of *mer*- $\text{CrCl}_3(\text{thf})_3$  (Figure 3c vs. Figure 3e,f). This observation, along with the mismatched EA data, creates uncertainty about the structure and composition of the purchased  $\text{CrCl}_3(\text{thf})_3$  as well as of the one prepared by the reported method. The solid deposited in the reaction pot of  $\text{CrCl}_2(\text{OH})(\text{H}_2\text{O})_2$  and  $\text{Me}_3\text{SiCl}$  (6 eq) showed a large signal at  $2\theta = 11.6^\circ$  along with the signals observed for the  $\text{CrCl}_3(\text{thf})_3$  samples (Figure 3d). The electron paramagnetic resonance (EPR) spectrum of  $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$  showed a strong signal at  $g = 1.98$ , while relatively weak signals were observed for the  $\text{CrCl}_3(\text{thf})_3$  samples; in addition, the signal patterns were completely different for the two samples (Figure 4). In thermogravimetry analysis (TGA) of  $\text{CrCl}_3(\text{thf})_3$ , roughly four stages of the weight loss were observed (30%, 50%, 60%, and 84% at 170 °C, 215 °C, 300 °C, and 1000 °C, respectively), while three stages of the weight loss were roughly observed for  $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$  (35%, 53%, and 73% at 220 °C, 310 °C, and 1000 °C, respectively).



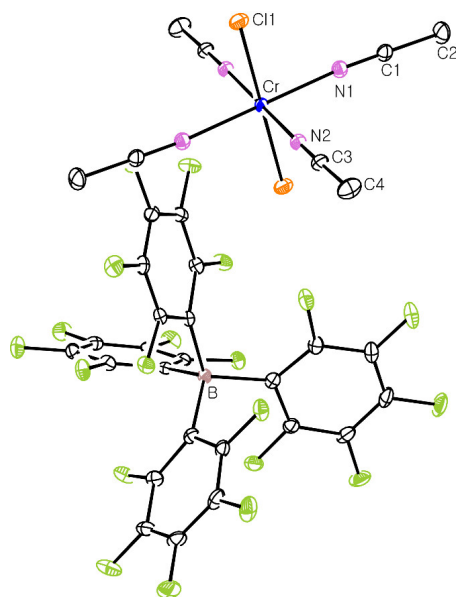
**Figure 3.** X-ray powder diffraction (XRD) patterns of  $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$  calculated from cif file (a) and measured (b) and those of  $\text{CrCl}_3(\text{thf})_3$  calculated from cif file (c), obtained from the reaction ' $\text{CrCl}_2(\text{OH})(\text{H}_2\text{O})_2 + \text{Me}_3\text{SiCl}$  (6 eq)'<sup>(d)</sup>, obtained from the reaction ' $\text{CrCl}_3 \cdot 6\text{H}_2\text{O} + \text{Me}_3\text{SiCl}$  (60 eq)'<sup>(e)</sup>, and purchased (f).





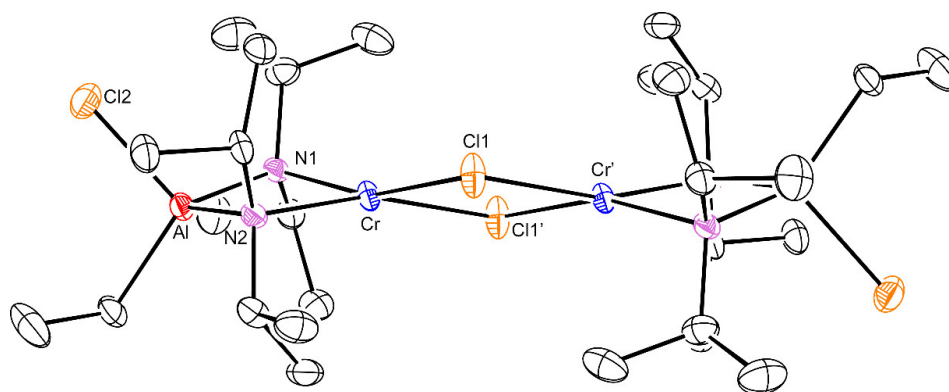
**Figure 4.** EPR spectra of  $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$  and the commercial  $\text{CrCl}_3(\text{thf})_3$ .

Many attempts to grow single crystals of  $[(\text{CH}_3\text{CN})_4\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  have been unsuccessful when  $[(\text{CH}_3\text{CN})_4\text{Ag}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  was reacted with the purchased  $\text{CrCl}_3(\text{thf})_3$  or the one prepared through the reaction of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  and excess  $\text{Me}_3\text{SiCl}$  (60 eq) without the evacuation step (Scheme 1) [38]. However, single crystals suitable for X-ray crystallography could be obtained when  $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$  was reacted with  $[(\text{CH}_3\text{CN})_4\text{Ag}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ . The structure determined by X-ray crystallography is shown in Figure 5. By reacting well-defined  $[(\text{CH}_3\text{CN})_4\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  with a  $i\text{PrN}\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-Si}(\text{nBu})_3)_2\}_2$  ligand [37], a high-quality Cr complex  $[i\text{PrN}\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-Si}(\text{nBu})_3)_2\}_2\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  was produced, which showed extremely high activity in the ethylene tetramerization reaction (activity: 6600 kg/g-Cr/h; selectivity: 1-octene—74.7%, 1-hexene—7.5%, cyclic-C6—3.8%, C10+—13.8%, PE—0.2%; reaction conditions: 34 bar ethylene, 235 mL methylcyclohexane, 0.45 mmol Cr catalyst, 90 mmol  $(i\text{Bu})_3\text{Al}$ , 40 °C, 30 min). The Cr complex  $[i\text{PrN}\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-Si}(\text{nBu})_3)_2\}_2\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  is highly soluble in methylcyclohexane, which is advantageous in handling and operating the tetramerization reaction, and there is no way for purification, necessitating a high-quality Cr precursor  $[(\text{CH}_3\text{CN})_4\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  as well as high-quality ligand  $i\text{PrN}\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-Si}(\text{nBu})_3)_2\}_2$  to ensure consistently high activity.



**Figure 5.** X-ray structure of  $[(\text{CH}_3\text{CN})_4\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ . Selected bond distances (Å) and angles (°): Cr-N1, 2.025(3); Cr-N2, 2.018(3); Cr-Cl1, 2.2804(9); Cr-N2-C, 178.8(3); and Cr-N1-C, 175.5(3).

In previous studies, we encountered a similar problem possibly caused by the use of impure  $\text{CrCl}_3(\text{thf})_3$ . In the reaction of  $\text{Li}^+[\text{Et}_2\text{Al}(\text{N}(\text{iPr})_2)_2]^-$  and  $\text{CrCl}_3(\text{thf})_3$ , solids were isolated; however, their structure could not be determined by X-ray crystallography. The product was tentatively considered to be  $[\text{Et}_2\text{Al}(\text{N}(\text{iPr})_2)_2]\text{CrCl}_2$  [48]. However, single crystals were obtained when well-defined  $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$  replaced the impure  $\text{CrCl}_3(\text{thf})_3$ , enabling structure determination by X-ray crystallography. The complex isolated from the reaction of  $\text{Li}^+[\text{Et}_2\text{Al}(\text{N}(\text{iPr})_2)_2]^-$  and  $\text{CrCl}_3(\text{thf})_3$  was not a Cr(III) complex  $[\text{Et}_2\text{Al}(\text{N}(\text{iPr})_2)_2]\text{CrCl}_2$  but a Cr(II) complex  $[\{\text{Et}(\text{Cl})\text{Al}(\text{N}(\text{iPr})_2)_2\}\text{Cr}(\mu\text{-Cl})_2]$  (Figure 6).



**Figure 6.** X-ray structure of  $[\{\text{Et}(\text{Cl})\text{Al}(\text{N}(\text{iPr})_2)_2\}\text{Cr}(\mu\text{-Cl})_2]$ . Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ): Cr–Cl1, 2.4212; Cr–N1, 2.141(6); Cr–N2, 2.119(6); Al–N1, 1.925(6); Al–N2, 1.953(6); Al–Cl2, 2.163(3); Cr–Cr', 3.578(2); N1–Cr–N2, 84.3(2); Cl–Cr–Cl', 83.96(8); N1–Al–N2, 95.0(3); and angle between N1–Cr–N2 and Cl–Cr–Cl' planes, 25.1(1).

### 3. Materials and Methods

#### 3.1. General Remarks

All manipulations were performed in an inert atmosphere using a standard glove box and Schlenk techniques.  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  were stirred over  $\text{CaH}_2$  and transferred to a reservoir under vacuum. Toluene, hexane, and THF were distilled from benzophenone ketyl. EAs were carried out at the Analytical Center, Ajou University. CW X-band EPR spectra were collected at room temperature on an EMX plus 6/1 spectrometer (Bruker, Billerica, MA, USA) with experimental parameters of 1 mW microwave power, 10 G modulation amplitude, and 3 scans at KBSI Western Seoul Center Korea. HP-XRD data were obtained on a D/max-2500V/PC (Rigaku, Akishima, Japan) equipped with a  $\text{Cu K}\alpha$  radiation source ( $\lambda = 0.15418 \text{ nm}$ ).

#### 3.2. $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$

A Schlenk flask containing crystalline solid  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (10.0 g, 37.5 mmol) was immersed in an oil bath at a temperature of  $40^\circ\text{C}$  and then evacuated under full vacuum for 1 h. Under evacuation, the bath temperature was raised to  $100^\circ\text{C}$  over an hour and then maintained at  $100^\circ\text{C}$  for 4 h. As volatiles were removed, the crystalline solid changed to an amorphous powder and the color of the solid gradually changed from dark green to light green, light gray, and finally light purple. The weight reduced from 10.0 to 6.39 g by the removal of volatiles. Cold THF (32 g,  $-30^\circ\text{C}$ ) was added to dissolve the remaining solid. By dissolution, heat was generated, and a dark-purple solution was obtained. Some insoluble portion was filtered off, and then,  $\text{Me}_3\text{SiCl}$  (24.5 g, 225 mmol) was added to the filtrate. Stirring the solution overnight led to the deposition of a purple solid. The solid was isolated via filtration and washed with THF (10 mL) and hexane (10 mL). The isolated solid (6.60 g) was placed in a large vial ( $\sim 70 \text{ mL}$  size) and  $\text{CH}_2\text{Cl}_2$  (53 g) was added to dissolve the solid. When the vial was placed inside a closed chamber ( $\sim 250 \text{ mL}$  size) containing methylcyclohexane ( $\sim 15 \text{ mL}$ ),  $\text{CH}_2\text{Cl}_2$  was slowly evaporated and purple crystals were deposited within 24 h, which were isolated by decantation (4.55 g, 69%).

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

A solution of  $[(\text{CH}_3\text{CN})_4\text{Ag}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  (7.789 g, 8.189 mmol) in acetonitrile (17.3 g) was added to a suspension of  $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$  (2.478 g, 8.189 mmol) in acetonitrile (22.6 g). After stirring overnight at 60 °C, precipitated AgCl was removed by filtration and an olive-green solution was obtained. The solvent was removed using a vacuum line to obtain an olive-green solid (7.71 g). The isolated solid (20.0 mg) and 9-methylanthracene (20.0 mg) were dissolved in THF- $d_8$ , and the  $^1\text{H}$  NMR spectrum of the solution was recorded to count the number of  $\text{CH}_3\text{CN}$  molecules per each Cr atom, which was 4.1. The yield was 97% based on the formula  $[(\text{CH}_3\text{CN})_{4.1}\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ . Single crystals suitable for X-ray crystallography were grown in  $\text{CH}_2\text{Cl}_2$ ; a vial containing  $[(\text{CH}_3\text{CN})_4\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  (100 mg) in  $\text{CH}_2\text{Cl}_2$  (1.0 g) was placed inside a closed chamber containing methylcyclohexane to deposit crystals.

### 3.4. $[\text{iPrN}\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-Si}(\text{nBu})_3)_2\}_2\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$

A solution of  $\text{iPrN}\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-Si}(\text{nBu})_3)_2\}_2$  (9.50 g, 7.78 mmol) in  $\text{CH}_2\text{Cl}_2$  (120 g) was added dropwise to a solution of  $[(\text{CH}_3\text{CN})_{4.1}\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  (7.55 g, 7.781 mmol) in  $\text{CH}_2\text{Cl}_2$  (46 g). Upon addition, the color of the solution changed immediately from olive-green to bluish-green. After stirring for 2.5 h, the solvent was completely removed using a vacuum line. The residue was dissolved in a minimal amount of methylcyclohexane (~5 mL), and the solvent was removed using a vacuum line. This procedure was repeated once more to remove any residual  $\text{CH}_3\text{CN}$  and  $\text{CH}_2\text{Cl}_2$  completely. The residue (15.7 g, 100%) was dissolved in methylcyclohexane (141.3 g) to obtain a 10 wt% solution, which was used for ethylene tetramerization.

### 3.5. $[\{\text{Et}(\text{Cl})\text{Al}(\text{N}(\text{iPr})_2)_2\}\text{Cr}(\mu\text{-Cl})]_2$

$[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$  (0.312 g, 1.03 mmol) was added to a solution of  $\text{Li}^+[\text{Et}_2\text{Al}(\text{N}(\text{iPr})_2)_2]^-$  (0.302 g, 1.03 mmol) in toluene (4.5 mL) at  $-30$  °C. The mixture was stirred for 8 h at room temperature. The color of the solution changed from dark brown to deep greenish-blue, and LiCl precipitated. The solvent was removed using a vacuum line, and the residue was dissolved in hexane (30 mL). After removal of LiCl via filtration, the filtrate was concentrated to ~10 mL and allowed to stand at  $-30$  °C for 2 days. Blue crystals were deposited (0.178 g, 45%). A second crop of blue crystals was obtained from the mother liquor (0.028 g, 7%).

### 3.6. X-ray Crystallography

Specimens of suitable quality and size were selected, mounted, and centered in the X-ray beam using a video camera. Reflection data were collected at 100 K on an APEX II CCD area diffractometer (Bruker, Billerica, MA, USA) using graphite-monochromated Mo K- $\alpha$  radiation ( $\lambda = 0.7107$  Å). The hemisphere of the reflection data was collected as  $\varphi$  and  $\omega$  scan frames at  $0.5^\circ$  per frame and an exposure time of 10 s per frame. The cell parameters were determined and refined using the SMART program. Data reduction was performed using the SAINT software. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program. The structure was solved by direct methods and refined by the full matrix least-squares method using the SHELXTL package and olex2 program with anisotropic thermal parameters for all non-hydrogen atoms.

Crystallographic data for  $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$  (CCDC# 2044805) that were used in all calculations are as follows:  $\text{C}_8\text{H}_{15.5}\text{Cl}_3\text{CrO}_2$ ,  $M = 302.05$ , triclinic,  $a = 6.8070(8)$ ,  $b = 9.3170(11)$ ,  $c = 10.3192(13)$  Å,  $\alpha = 108.070(5)^\circ$ ,  $\beta = 96.448(5)^\circ$ ,  $\gamma = 94.719(5)^\circ$ ,  $V = 613.47(13)$  Å<sup>3</sup>, space group  $P\bar{1}$ ,  $Z = 2$ , and 2285 unique ( $R(\text{int}) = 0.0505$ ). The final  $wR_2$  was 0.1251 ( $I > 2\sigma(I)$ ).

Crystallographic data for  $[(\text{CH}_3\text{CN})_4\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^- \cdot 2(\text{CH}_2\text{Cl}_2)$  (CCDC# 2044806) that were used in all calculations are as follows:  $\text{C}_{34.5}\text{H}_{17}\text{BCl}_7\text{CrF}_{20}\text{N}_4$ ,  $M = 1178.48$ , monoclinic,  $a = 12.9472(4)$ ,  $b = 8.2694(3)$ ,  $c = 21.7555(8)$  Å,  $\beta = 99.8523(18)^\circ$ ,  $V = 2294.91(14)$



$\text{\AA}^3$ , space group  $P2_1/c$ ,  $Z = 2$ , and 4409 unique ( $R(\text{int}) = 0.0285$ ). The final  $wR_2$  was 0.1594 ( $I > 2\sigma(I)$ ).

Crystallographic data for  $[\{\text{Et}(\text{Cl})\text{Al}(\text{N}(\text{iPr})_2)_2\}\text{Cr}(\mu\text{-Cl})_2]$  (CCDC# 2044807) that were used in all calculations are as follows:  $\text{C}_{28}\text{H}_{66}\text{Al}_2\text{Cl}_4\text{Cr}_2\text{N}_4$ ,  $M = 758.60$ , monoclinic,  $a = 10.2937(2)$ ,  $b = 12.8707(3)$ ,  $c = 14.7815(3)$   $\text{\AA}$ ,  $\beta = 96.5009(18)^\circ$ ,  $V = 1945.77(7)$   $\text{\AA}^3$ , space group  $P2_1/n$ ,  $Z = 2$ , and 3675 unique ( $R(\text{int}) = 0.1527$ ). The final  $wR_2$  was 0.0909 ( $I > 2\sigma(I)$ ).

#### 4. Conclusions

The commonly used  $\text{CrCl}_3(\text{thf})_3$  is impure obtaining as an irregular solid with no possibility of recrystallization. Another form of the THF adduct of  $\text{CrCl}_3$  (i.e.,  $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$ ) was facilely prepared in this work. The structure of  $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$  determined by X-ray crystallography agreed well with the XRD patterns and the C content of the bulk. Using well-defined  $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$  instead of the impure  $\text{CrCl}_3(\text{thf})_3$  as a starting material, the activity of the ethylene tetramerization catalyst  $[\text{iPrN}\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-Si}(\text{nBu})_3)_2\}_2\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  was consistent and extremely high (6600 kg/g-Cr/h), and some Cr complexes (e.g.,  $[(\text{CH}_3\text{CN})_4\text{CrCl}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  and  $[\{\text{Et}(\text{Cl})\text{Al}(\text{N}(\text{iPr})_2)_2\}\text{Cr}(\mu\text{-Cl})_2]$ ) whose structure determination had failed previously could be isolated as high-quality crystals, enabling structure determination by X-ray crystallography. We strongly suggest the use of well-defined  $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$  instead of the impure  $\text{CrCl}_3(\text{thf})_3$  as a Cr source in the synthesis of organometallic and coordination compounds of Cr.

#### 5. Patents

A patent was applied on this study (Ajou University, Chromium Compound and Method for Preparing the Same. Kr 10-2020-0052494, 29 April 2020).

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**Data Availability Statement:** The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Conflicts of Interest:** Ajou University (inventors: D. G. Lee, J. W. Baek, and B. Y. Lee) have applied for a patent covering this research.

**Sample Availability:** Samples of  $[\text{CrCl}_2(\mu\text{-Cl})(\text{thf})_2]_2$  are available from the Precious Catalysts Inc.; cglee@s-pci.com (C.G.L.).

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