

[(NHC)CrCl(μ -Cl)(THF)]₂ and (NHC)₂CrCl₂ (NHC = 1,3-Diisopropyl-4,5-dimethylimidazole-2-ylidene): Syntheses, Structures, and Polymerization Activities^①

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ABSTRACT The preparation of divalent chromium N-heterocyclic carbene (NHC, 1,3-diisopropyl-4,5-dimethylimidazole-2-ylidene) compounds is reported. The reaction of 1:1 molar ratio of NHC with CrCl₂ led to an isolation of [(NHC)CrCl(μ -Cl)(THF)]₂ (**1**), while that of 2:1 ratio resulted in the formation of (NHC)₂CrCl₂ (**2**). **1** can be considered as an intermediate in the formation of **2** and further converted into **2** by the addition of another equiv. of NHC. The reaction of **2** with CpNa afforded an ion pair compound [(NHC)₂CrCp]⁺[Cp]⁻ (**3**), indicating a strong coordination ability of NHC supplanting one of the ionic Cr-Cp bonding. In combination of methylalumoxane (MAO) as cocatalyst **1** and **2** both are active for catalyzing ethylene polymerization.

Keywords: chromium(II) compounds, N-heterocyclic carbene, crystal structure, polymerization activity

1 INTRODUCTION

N-heterocyclic carbene (NHC) was initially synthesized as imidazolium salt^[1], and until 1991 it was isolated as a stable monomer by Arduengo and coworkers^[2]. Due to the uniquely electronic (strong σ donor and weak π acceptor) and steric (tunable N-substituents) properties, NHC can preferably form the metal in a low order of aggregations and coordinate numbers, and soon becomes the versatile and prolific ligands in catalysis in a multitude. Currently, it has been widely applied to prepare a variety of main-group, transition metal, and lanthanide complexes^[3 ~ 10].

Chromium-based complexes are of great commercial interest due to their catalytic property for olefin polymerization since the discovery of chromium oxide

catalysts (Philips catalyst) and supported organochromium catalysts (Union Carbide catalyst) which account for the production of nearly 40% of all the polyethylene resins throughout the world^[11 ~ 15]. The homogeneous chromium catalysts of Ziegler-Natta type are generally produced by coordination of organic ligand at Cr, forming the complexes soluble in organic solvents. As shown in scheme 1, such kind of complexes is principally of a mononuclear nature with the metal center in a relatively low coordination, allowing the functionalized reactions of X group to occur in the coordination polymerization of olefinic substrates. Recent years' distributions on this aspect have shown that the N-heterocyclic carbene is a good ligand for the preparation of these complexes. Several didentate (CC) and terdentate (CNC) NHC chromium complexes have

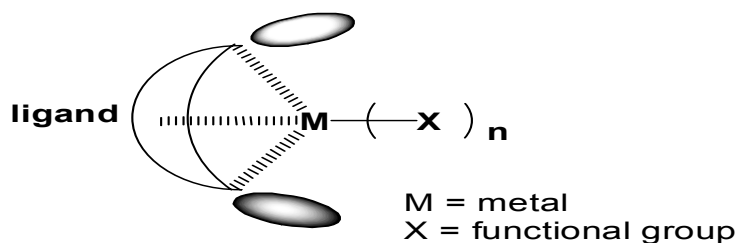
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been reported and successfully applied as catalyst for ethylene polymerization^[16, 17]. We present here that NHC can form inorganic CrCl₂ as two new adducts: **1** and **2**, by using different molar ratios of the starting materials. The metathesis reaction of **2** with CpNa

smoothly afforded an ion pair compound **3**. Subsequent ethylene polymerization investigation shows that **1** and **2** are active in the combination of methylalumoxane (MAO) cocatalyst and exhibit a better activity when compared to that of CrCl₂.



Scheme 1

2 EXPERIMENTAL

2.1 General procedures

All syntheses and manipulations were carried out on a dual-manifold Schlenk line or in an argon-filled MBraun glove box (typically < 1.2 ppm oxygen and moisture). Analytical grade organic solvents (toluene, hexane, THF, and diethyl ether) were predried over fine sodium wires for more than one week and then subjected to reflux with sodium/potassium benzophenone under nitrogen atmosphere prior to use. ¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were recorded on a Bruker Avance II 400 MHz spectrometer. IR spectra were recorded on a Nicolet Avatar 380 RT-IR spectrophotometer. Melting point was measured in a sealed glass tube using Büchi-540 instrument. Elemental analyses were performed on a Thermo Quest Italia SPA EA 1110 instrument. Commercially available reagents were purchased from Aldrich, Acros, Alfa-Assar, or Lvyin Chemical Co. NHC was prepared according to published procedures^[18].

2.2 Synthesis of [(NHC)CrCl(μ -Cl)(THF)]₂ (**1**)

A solution of NHC (0.34 g, 1.9 mmol) in THF (15 mL) was added to a suspension of CrCl₂ (0.23 g, 1.9 mmol) in THF (30 mL) at -30 °C. By stirring, the suspension turned blue soon. After stirring for 12 h, the solvent was removed under vacuum, and the residue was extracted into toluene (30 mL). The extract was concentrated (*ca.* 5 mL) and to it hexane

(5 mL) was added. The solution was stayed at room temperature for 2 d, and blue crystalline solid of **1** was formed. Yield: 0.56 g, 39%. m.p.: 180 °C. Anal. Calcd. (%) for C₃₀H₅₆Cl₄Cr₂N₄O₂ (*M_r* = 750.58): C, 48.00; H, 7.52; N, 7.46. Found (%): C, 47.19; H, 6.94; N, 7.04. IR (Nujol mull): 1628 (w), 1550 (w), 1463 (s), 1377 (s), 1232 (w), 1191 (w), 1136 (w), 1110 (w), 1066 (w), 966 (w), 890 (w), 720 (w), 662 (w), 537 (w) cm⁻¹. NMR: δ H 1.60 (br, 8 H, OCH₂CH₂), 5.03 (br, 8 H, OCH₂CH₂), 12.38 (br, 4 H, CHMe₂), 17.39 (br, 24 H, CHMe₂), 24.67 (br, 12 H, CMe) ppm.

2.3 Synthesis of (NHC)₂CrCl₂ (**2**)

A solution of NHC (1.43 g, 7.8 mmol) in THF (15 mL) was added to a suspension of CrCl₂ (0.49 g, 3.9 mmol) in THF (30 mL) at -30 °C. The suspension became purple quickly. After stirring for 12 h, the solvent was removed under vacuum, and the residue was extracted into toluene (40 mL). The extract was concentrated (*ca.* 10 mL) and then to it hexane (5 mL) was added. The purple crystalline solid of **2** was obtained by keeping the solution at room temperature for 2 d. Yield: 1.63 g, 86%. m.p.: 192 °C. Anal. Calcd. (%) for C₂₂H₄₀Cl₂CrN₄ (*M_r* = 483.48): C, 54.65; H, 8.34; N, 11.59. Found (%): C, 54.61; H, 7.96; N, 11.62. IR (Nujol mull): 1629 (m), 1463 (s), 1377 (m), 1104 (w), 960 (w), 902 (w), 745 (m), 742 (m), 573 (w) cm⁻¹. NMR: δ H 14.97 (br, 2 + 12 H, CHMe₂ + CHMe₂), 23.95 (br, 6 H, CMe) ppm.

2.4 Synthesis of [(NHC)₂CrCp]⁺[Cp]⁻ (**3**)

CpNa (0.83 mL, 2.27 M in THF) was added to a solution of **2** (0.43 g, 0.89 mmol) in THF (25 mL) at $-30\text{ }^{\circ}\text{C}$. The resulting solution rapidly changed its color from purple to dark brown. After stirring for 12 h, the solvent was removed under vacuum, and the residue was extracted into toluene (15 mL). The extract was concentrated (*ca.* 5 mL) and then to it hexane (10 mL) was added. X-ray quality single crystals of **3** were obtained after keeping the solution at $-10\text{ }^{\circ}\text{C}$ for one week. Yield: 0.36 g, 73%. m.p.: $139\text{ }^{\circ}\text{C}$. Anal. Calcd. (%) for $\text{C}_{32}\text{H}_{50}\text{CrN}_4$ ($M_r = 542.76$): C, 70.81; H, 9.29; N, 10.32. Found (%): C, 70.75; H, 9.10; N, 10.09. IR (Nujol mull): 1628 (m), 1463 (s), 1377 (s), 1358 (sh, s), 1232 (w), 1005 (w), 722 (m) cm^{-1} ; NMR: δ H 1.46, 1.70 (br, 5 + 5 H, C_5H_5), 26.5 (br, 4 + 24 H, $\text{CHMe}_2 + \text{CHMe}_2$), 28.3 (br, 12 H, CMe) ppm (Note: This compound has been reported, but prepared in another way. We prepare it here in a new synthetic route. The important analytic data shown together are due to the confirmation of this compound).

2.5 Crystallographic data collection and structural determination

X-ray quality crystals of compounds **1** and **2** were obtained by recrystallization from a mixture solvent of THF and hexane at room temperature, respectively, and mounted on a glass fiber using paratone oil. The data were collected on an Oxford Gemini S Ultra system. In all cases a graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) was used. Absorption corrections were employed by using the program CrysAlis (multi-scan). The structures were solved by direct methods (SHELXS-96) and refined against F^2 using SHELXL-97^[19, 20]. In general, the non-hydrogen atoms were located by difference Fourier synthesis and refined anisotropically, and hydrogen atoms were included using a riding mode with U_{iso} tied to U_{iso} of the parent atom unless otherwise specified. A summary of cell parameters, data collection, and structure solution and refinement is given in Table 1.

Table 1. Crystallographic Data for Compounds **1** and **2**

	1	2
Formula	$\text{C}_{15}\text{H}_{28}\text{Cl}_2\text{CrN}_2\text{O}$	$\text{C}_{22}\text{H}_{40}\text{Cl}_2\text{CrN}_4$
F_w	375.29	483.48
Temp. (K)	173(2)	173(2)
Crystal syst.	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$Pca2(1)$
a (\AA)	9.859(2)	21.8432(6)
b (\AA)	9.8836(11)	9.9629(2)
c (\AA)	10.6385(19)	11.4808(3)
α (deg)	104.746(12)	90
β (deg)	108.861(18)	90
γ (deg)	100.400(14)	90
V (\AA^3)	908.7(3)	2498.47(11)
Z	2	4
ρ_c (Mg/m^3)	1.372	1.285
μ (mm^{-1})	0.924	0.687
$F(000)$	792	1032
θ range (deg)	2.28~26	2.25~26.00
Index ranges	$-12 \leq h \leq 11$ $-12 \leq k \leq 11$ $-13 \leq l \leq 12$	$-26 \leq h \leq 26$ $-12 \leq k \leq 12$ $-14 \leq l \leq 14$
No. of reflns collected	7623	24185
No. of indep reflns (R_{int})	3493 (0.0309)	4888 (0.0361)
No. of data/restraints/params	3493/0/191	4888/1/274
GOF/F^2	0.940	1.036
R^a, wR^b ($I > 2\sigma(I)$)	0.0354, 0.0729	0.0301, 0.0629
R^a, wR^b (all data)	0.0585, 0.0773	0.0366, 0.0644
Largest diff. peak/hole ($\text{e}\cdot\text{\AA}^{-3}$)	0.449/-0.280	0.290/-0.285

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; ^b wR = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$$

2.6 Polymerization procedures

In a typical experiment, chromium compounds and MAO in toluene solution (40 mL) at 70 °C were exposed to ethylene at 18 bar. After 1 h, the poly-

merization mixture was quenched with acidic methanol. The polymer was collected by filtration and dried at 50 °C overnight to a constant weight. A summary of polymerization results is given in Table 3.

Table 3. Ethylene Polymerization Results Using Chromium Compounds

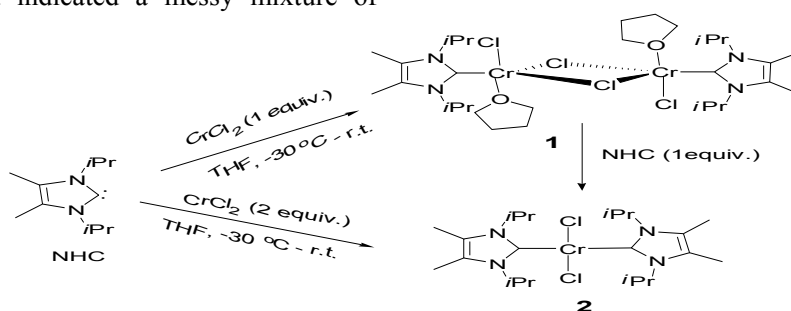
Run	Catalyst	Cocatalyst	Cr/Al	PE	Activity
1	CrCl ₂ (0.02)	MAO (5.3)	1 : 400	0.077	0.213
2	CrCl ₂ (0.02)	MAO (10.9)	1 : 800	0.588	1.633
3	1 (0.02)	MAO (5.3)	1 : 400	0.136	0.378
4	2 (0.02)	MAO (1.3)	1 : 100	0.150	0.417
5	2 (0.02)	MAO (2.6)	1 : 200	0.623	1.731
6	2 (0.02)	MAO (5.3)	1 : 400	0.729	2.025
7	2 (0.02)	MAO (10.6)	1 : 800	1.064	2.944
8	2 (0.02)	MAO (15.9)	1 : 1200	0.865	2.403
9	2 (0.02)	MAO (19.9)	1 : 1500	0.928	2.577

Conditions: polymerization pressure, 18 bar; temperature, 70 °C; time, 1 h, solvent, toluene (40 mL); MAO, density, 0.872 g/mL, and weight percentage, 4.65%

3 RESULTS AND DISCUSSION

As shown in Scheme 2, when the molar ratio of NHC and CrCl₂ was controlled at 1:1, a quick color change of the reaction suspension to blue was observed, and finally a blue crystalline solid of **1** was cropped. However, the yield was relatively low (39%). Further addition of 1 equiv. of NHC to the forming repeated reaction turned the solution color into purple, affording another type product **2** as a purple crystalline solid in high yield (86%). A direct reaction of NHC and CrCl₂ in a molar ratio of 2:1 expectedly gave the same result. Therefore, we may infer that the low yield formation of **1** from the 1:1 reaction of NHC and CrCl₂ could imply a somewhat kinetic formation of **2** although the further isolation of **2** was not successful due to an oily residue that was obtained after the separation of **1** and indicated a messy mixture of

products by proton NMR spectral analysis. An excess of NHC was used in an attempt to check out the formation of higher order of NHC:CrCl₂ compound, and **2** was still formed with more NHC left unreacted. These experimental results indicate that in the reaction system of NHC and CrCl₂, **1** can be regarded as an intermediate in the formation of **2**, and NHC has a stronger σ donor coordination ability to further replace THF. The steric character of NHC led to a dissociation of **1** and a formation of **2** as a monomer. Compounds **1** and **2** are both soluble in THF and toluene, but sparingly soluble in hexane. **1** melts at 180 °C and **2** at 192 °C, suggesting their thermal stability. They have been characterized by IR and ¹H NMR spectroscopy, X-ray crystallography, and elemental analysis. The proton NMR data gave broad resonances, indicative of paramagnetic property of **1** and **2**.



Scheme 2. Syntheses of **1 and **2****

The structural analysis confirmed a different formation between **1** and **2**. The structures of **1** and **2** are shown in Figs. 1 and 2, respectively. Important bond lengths and bond angles are listed in Table 2. Compound **1** is a dimer, and the coordination of each Cr atom is completed by one NHC, one THF, one terminal Cl, and two μ -Cl atoms, forming a distorted square-pyramidal geometry. The Cr–C bond in 2.134(2) Å is comparable to those dative bonds found in Cr(II) complexes (NHC)Cr(Cp)Ph^[21] (2.123(1) Å) and [(NHC)₂CrCp]⁺[Cp]⁻ (2.091(2), 2.103(2) Å)^[22]. The Cr–O bond is 2.336(2) Å, and a little shorter distance appears in Cr(III) compound CrPh₃(THF)₃ (2.225(10) Å)^[23]. Probably due to the different ligands THF and NHC imposed at the Cr, the bridged Cr– μ -Cl

bond lengths (2.418(1) and 2.462(1) Å) are differed by 0.044 Å. These distances are longer than the terminal one (2.352(1) Å), but locate within those bridged ones in Cr(II) dimer $\{[(\text{Ph}_2\text{PCH}_2\text{SiMe}_2)\text{N}]\text{Cr}\}_2(\mu\text{-Cl})_2$ (2.397(3) and 2.546(3) Å)^[24]. Compound **2** is a monomer with a four-coordinate Cr center in a nearly square-planar geometry. The Cr–Cl bond distances (2.346(1) and 2.352(1) Å) are close to the terminal one in **1**, whereas the Cr–C lengths (2.168(2) and 2.169(2) Å) are a little longer when compared to that in **1**. The Cl–Cr–Cl (174.05(3)°) and C–Cr–C (172.74(8)°) bond angles slightly deviate from the linear one, showing an ideal *trans*-array of two NHC and two Cl⁻ ligands at the Cr center.

Table 2. Selected Bond Lengths (Å) and Bond Angle (°) for Compounds **1** and **2**

1					
Bond	Dist	Bond	Dist	Bond	Dist
Cr(1)–C(1)	2.135(2)	Cr(1)–O(1)	2.3361(18)	Cr(1)–Cl(1)	2.3516(7)
Cr(1)–Cl(2)	2.4188(7)	Cr(1)–Cl(2A)	2.4616(9)	Cr(1A)–Cl(2)	2.4116(9)
Angle	(°)	Angle	(°)	Angle	(°)
C(1)–Cr(1)–O(1)	108.63(8)	C(1)–Cr(1)–Cl(1)	93.68(6)	O(1)–Cr(1)–Cl(1)	92.56(5)
C(1)–Cr(1)–Cl(2)	87.36(6)	O(1)–Cr(1)–Cl(2)	92.87(4)	Cl(1)–Cr(1)–Cl(2)	173.82(3)
C(1)–Cr(1)–Cl(2A)	159.58(6)	O(1)–Cr(1)–Cl(2A)	90.14(5)	Cl(1)–Cr(1)–Cl(2A)	93.41(3)
2					
Bond	Dist	Bond	Dist	Bond	Dist
Cr(1)–C(1)	2.168(2)	Cr(1)–C(21)	2.169(2)	Cr(1)–Cl(1)	2.3463(8)
Cr(1)–Cl(2)	2.3524(8)				
Angle	(°)	Angle	(°)	Angle	(°)
C(1)–Cr(1)–C(21)	172.74(8)	Cl(1)–Cr(1)–Cl(2)	174.05(3)	C(1)–Cr(1)–Cl(1)	90.73(7)
C(1)–Cr(1)–Cl(2)	89.73(7)	C(21)–Cr(1)–Cl(1)	90.50(6)	C(21)–Cr(1)–Cl(2)	90.15(6)

Symmetric operation: #1: $-x-2, -y+2, -z+1$

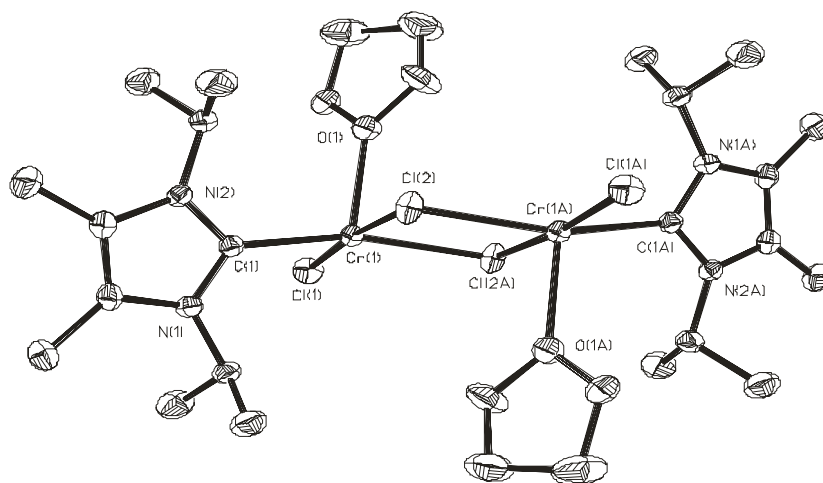


Fig. 1. Crystal structure of **1** at 50% thermal ellipsoids. The hydrogen atoms were omitted for clarity

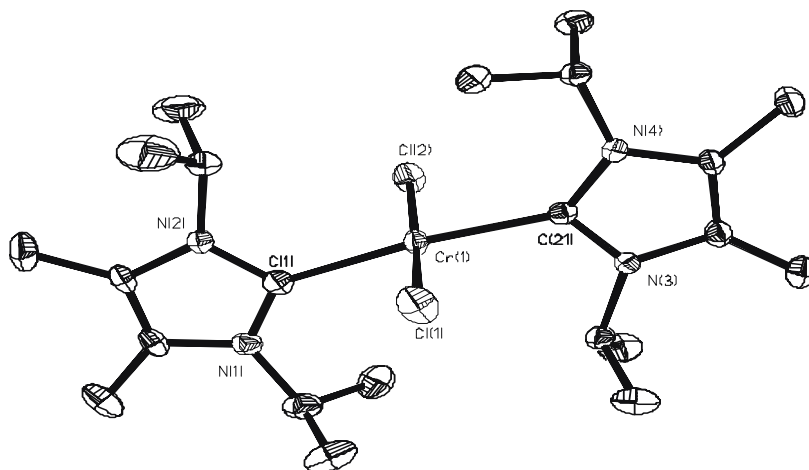
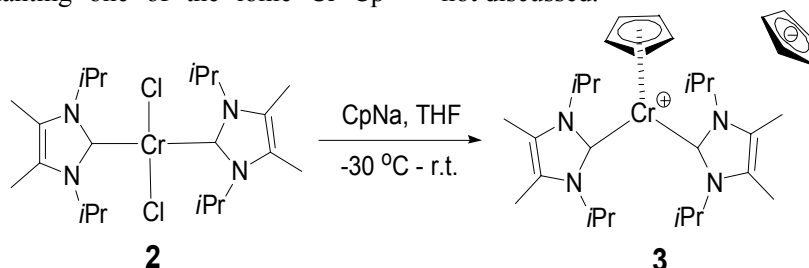


Fig. 2. Crystal structure of **2** at 50% thermal ellipsoids. The hydrogen atoms were omitted for clarity

Further metathesis reaction of **2** with CpNa was carried out, resulting in an ion pair compound [(NHC)₂CrCp]⁺[Cp]⁻ (Scheme 3). This is a known complex obtained by Cowley and Jones *et al.*^[22] as a novel 14-electron chromocene cation product from a reaction of CrCp₂ with NHC. The formation of such type compound indicates a strong coordination capacity of NHC supplanting one of the ionic Cr–Cp

bondings. Although this compound has been structurally characterized, we do perform the structural authentication again due to that it was formed from a different reaction system and other means were not able to clearly identify it with respect to its paramagnetic character. The crystal structure is shown in Fig. 3 for a view and the related structural details are not discussed.



Scheme 3. Synthesis of **3**

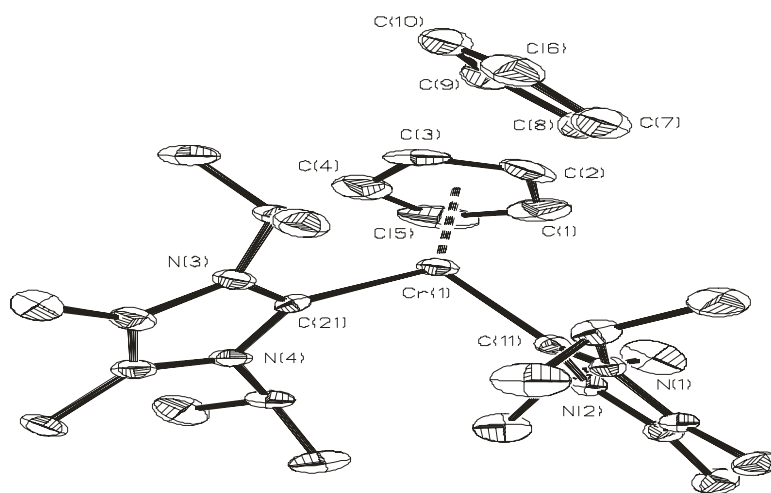


Fig. 3. Crystal structure of **3** at 50% thermal ellipsoids. The hydrogen atoms were omitted for clarity

In the presence of excess MAO, **1** and **2** catalyzed the polymerization of ethylene. As shown in Table 3, with an increase of MAO loading, the activity using **2** was improved and reached to the maximum (2.94 g/mmole·h-bar, run 7) at the Cr/Al molar ratio of 1:800, and then went a little down (2.403 and 2.577 g/mmole·h-bar, runs 8-9). However, lower activity was observed for **1** (0.378 g/mmole·h-bar, run 3). In the meantime, a blank test using CrCl₂ only was also performed for comparison. Under similar conditions, **1** and **2** are more active than CrCl₂ when treated with the same Cr/Al ratio of 1:400 (runs 1, 3 and 6). This indicates that the use of NHC to coordinate with CrCl₂ improves the solubility of the catalyst thus enhancing the interaction between catalyst and cocatalyst to form the active sites. Furthermore, the NHC may well support the Cr center for catalyzing the ethylene polymerization, and such

double coordination shows a more efficient influence, as evidenced with a higher activity achieved by **2** than that by **1**.

4 CONCLUSION

In summary, based on the unique properties, N-heterocyclic carbene form CrCl₂ as, to our search in the CCDC database, two new compounds of **1** and **2**. **1** can be regarded as an intermediate in the formation of **2**. **1** and **2** exhibit a better activity in ethylene polymerization when compared to CrCl₂ in the presence of MAO, showing the advantage by using NHC as ligand in gaining the solubility and stability issues of the formed compounds as catalysts. Further work in an attempt to prepare other NHC-stabilized organochromium compounds is in process in our lab.

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