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# Coordination chemistry of the activation of [(triazacyclohexane)CrCl<sub>3</sub>] with [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and AlR<sub>3</sub>

Randolf D. Köhn<sup>a,\*</sup>, David Smith<sup>a</sup>, Mary F. Mahon<sup>a</sup>, Martina Prinz<sup>b</sup>,  
Shahram Mihan<sup>c</sup>, Gabriele Kociok-Köhn<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Bath, Bath BA2 7AY, UK

<sup>b</sup> BASF AG, Research Laboratory, D-67056 Ludwigshafen, Germany

<sup>c</sup> Basell Polyolefins GmbH, Research Laboratory, D-67056 Ludwigshafen, Germany

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## Abstract

Complexes of *N*-substituted 1,3,5-triazacyclohexanes with CrCl<sub>3</sub> form 1:1 adducts with [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] with increased solubility in toluene. Addition of Al<sup>i</sup>Bu<sub>3</sub> leads to free PhNMe<sub>2</sub> and a complex with [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup> weakly coordinated to chromium via a *meta*-fluorine atom. This complex can polymerise and/or trimerise olefins similar to methyl aluminoxane activated complexes. Decomposition of the active complex involves transfer of the triazacyclohexane to aluminium leading to [(triazacyclohexane)Al<sup>i</sup>Bu<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and [(arene)<sub>2</sub>Cr][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. These chromium(I) complexes have been characterised by X-ray crystallography and prove that chromium is reduced to the oxidation state +I during the catalysis.

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**Keywords:** Chromium; Olefin trimerisation; Arene complexes

## 1. Introduction

Several transition metal systems have been found over the past 50 years that can catalyse the polymerisation and oligomerisation of olefins. Heterogeneous Ziegler-Natta systems based on early transition metals are the most successful and produce a large variety of polyolefins. Homogeneous single site systems, initially the group IV metallocenes but later with many different ligands and metals, have been developed which are able to produce highly stereo regular polymers and have become useful industrial catalysts. The study of these homogeneous systems has tremendously improved the detailed understanding of the catalytic mechanism. Generally the transition metal complexes are treated with a co-catalyst to become active. The most commonly used co-catalyst is methyl aluminoxane (MAO).

Alternatively, other alkylating agents like AlR<sub>3</sub> in combination with alkyl-abstracting agent like B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or anilinium or trityl salts of weakly coordinating anions like [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup> can be used. These co-catalysts have the advantage of producing well defined anions that allow the spectroscopic or crystallographic investigation of the catalysts.

The heterogeneous Phillips catalysts [1–5] based on CrO<sub>3</sub>/SiO<sub>2</sub> for the polymerisation of ethylene have been known as long as the Ziegler-Natta systems and they still produce a large fraction of the world production of HDPE (> 7 million ton per annum) [6,7]. This system has many unusual features compared to the other transition metal catalysts and little is known about its active species and mechanism [8–10]. After the initial report by Briggs [11], some homogeneous chromium systems have been developed that are able to catalyse the unusual selective trimerisation of ethylene. These systems generally consist of some soluble chromium complex, aluminium alkyls and some amine, mostly pyrroles [12] or more recently PNP ligands [13]. The

\* Corresponding author. Tel.: +44-1225-38-3305; fax: +44-1225-38-6231.

E-mail address: [r.d.kohn@bath.ac.uk](mailto:r.d.kohn@bath.ac.uk) (R.D. Köhn).

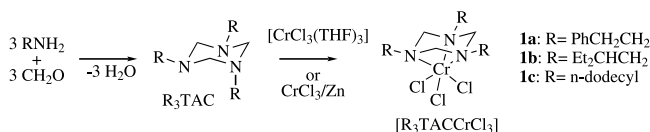
increasing demand for 1-hexene has sparked a growing interest in these selective trimerisation catalysts.

However, little is known about the active species in these complex mixtures largely due to the difficulty of obtaining useful NMR spectra of these highly paramagnetic compounds. Briggs [11] and others have proposed a mechanism via metallacycles analogous to Scheme 2 and Jolly and co-workers [14] were able to support the involvement of metallacyclopentane and metallacycloheptane complexes. Although oxidative addition of the olefins and reductive elimination of the trimer are required by this mechanism, no oxidation states of chromium other than +III have been proven in the catalytic cycle, and redox steps via Cr(I)/Cr(III) or Cr(II)/Cr(IV) have been proposed. A similar mechanism has recently been found for titanium systems [15,16] or TaCl<sub>3</sub>Me<sub>2</sub> [17] and a recent computational study of the latter system confirms a mechanism via metallacycles and two oxidation states [18].

For several years we have been investigating the coordination chemistry of *N*-substituted 1,3,5-triazacyclohexanes (R<sub>3</sub>TAC) [19–23]. Our results on the coordination chemistry of R<sub>3</sub>TAC show that complexes with low steric demand by the ligand and the misdirected nitrogen lone pairs due to the small N–metal–N angle of 60–65° can be formed.

The triazacyclohexane complexes of CrCl<sub>3</sub> (Scheme 1) can be activated with MAO [25] or [PhNM<sub>2</sub>H]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup> (DMAB) followed by trialkylaluminium. Depending on the substituents, the catalyst can polymerise or selectively trimerise ethylene and, for the first time, also trimerise  $\alpha$ -olefins. Activities of up to 800 kg mol Cr<sup>−1</sup> h<sup>−1</sup> with MAO or up to 2800 kg mol Cr<sup>−1</sup> h<sup>−1</sup> with DMAB/Al<sup>*i*</sup>Bu<sub>3</sub> can be obtained. Thus, the activity is comparable to that of the heterogeneous Phillips catalyst (500–3000 kg mol Cr<sup>−1</sup> h<sup>−1</sup>) and more active chromium catalysts have only been obtained with Cp-based systems [10,26] (up to 20 000 kg mol Cr<sup>−1</sup> h<sup>−1</sup>).

A single mononuclear chromium(III) complex is observed during the catalysis, probably a metallacyclopentane complex. The observation of two broadened and shifted signals in <sup>2</sup>H-NMR studies with a ring-deuterated ligand proves that the triazacyclohexane is coordinated to the paramagnetic chromium in the active complex. The kinetic data can be fitted to rate laws derived from the metallacyclic mechanism outlined in Scheme 2.



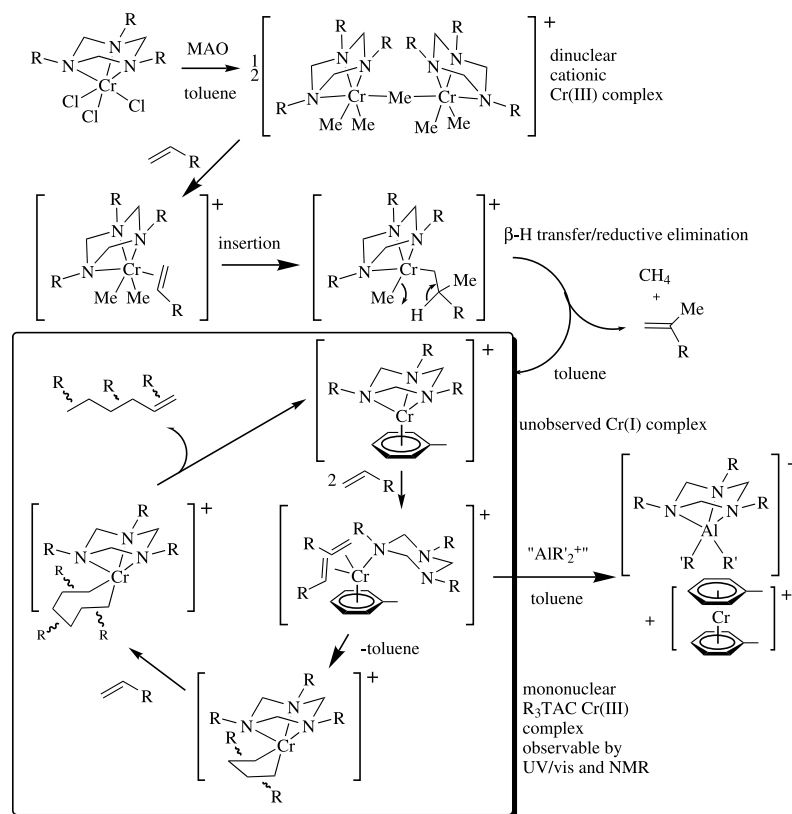
Scheme 1. Syntheses of the complexes 1.

The much slower trimerisation of  $\alpha$ -olefins especially suffers from the relatively fast deactivation of the system. To our knowledge, no alternative system is yet known for the catalytic trimerisation of  $\alpha$ -olefins. Therefore, a detailed understanding of the activation and deactivation processes is mandatory for the development of better catalysts. Here we describe a detailed investigation of the activation with DMAB/Al<sup>*i*</sup>Bu<sub>3</sub> and subsequent decomposition.

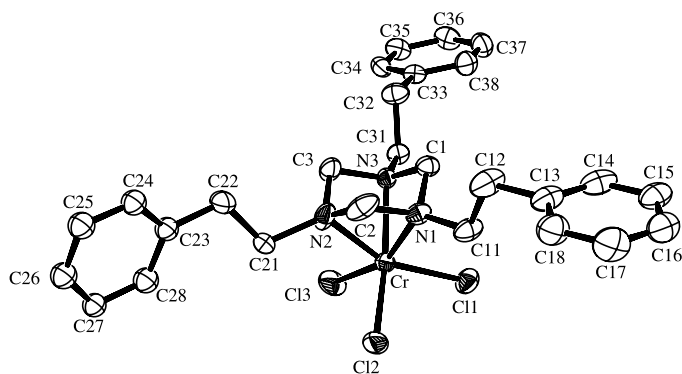
## 2. Results and discussion

The activation by DMAB/Al<sup>*i*</sup>Bu<sub>3</sub> is best performed in two steps. First [(R<sub>3</sub>TAC)CrCl<sub>3</sub>] is treated with one equivalent of DMAB in toluene or benzene. Even poorly soluble chromium complexes dissolve readily upon the addition of DMAB. This increased solubility greatly enhances the catalytic performance of many complexes. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of these solutions show severely broadened or unobservable signals for the aniline and significant broadening of the <sup>19</sup>F-NMR signals to 100–300 Hz. This indicates an anilinium adduct with a close contact to the paramagnetic chromium and ion pairing with the anion. For the cases R = PhCH<sub>2</sub>CH<sub>2</sub> (**2a**) and R = Et<sub>2</sub>CHCH<sub>2</sub> (**2b**) crystals were grown from the solution and analysed by X-ray crystallography. The crystal structure of **1a** as the precursor of the adduct was determined as well to investigate the effect of the anilinium adduct. The structures of **1a** and the cations in **2a** and **2b** are shown in Figs. 1–3 and selected bond distances and angles are given in Table 1.

Comparison of the data shows little significant change in the coordination environment of chromium upon adduct formation. More significantly the adduct formation changes the weak intermolecular hydrogen bonding network. In **1a**, contacts between hydrogen atoms of the triazacyclohexane ring and chloride atoms of neighbouring molecules are found (closest distance H3A···Cl1 2.84 Å) (and slightly longer contacts to other hydrogen atoms of neighbouring ligands) leading to an infinite weak hydrogen bonding network. Similar contacts are found in many other [(R<sub>3</sub>TAC)CrCl<sub>3</sub>] complexes [27]. In the anilinium adduct **2a**, two strong hydrogen bonds (H1A···Cl1 2.52 Å) form an isolated dinuclear unit (Fig. 2) with no additional H···Cl contacts at distances smaller than 3 Å. The bulkier *N*-substituents in **2b** prevent this close interaction and a zig-zag chain of much weaker contacts is found (H1B···Cl1 and H3B···Cl3 both 2.91 Å). Thus, engaging the chloride atoms in an anilinium adduct weakens the intermolecular contacts between the chromium complexes in the solid state and may be the cause for the observed increased solubility of the adducts.



Scheme 2. Proposed mechanism for the selective trimerisation [24].

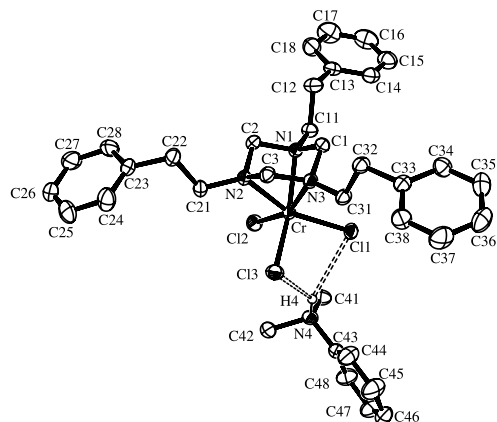
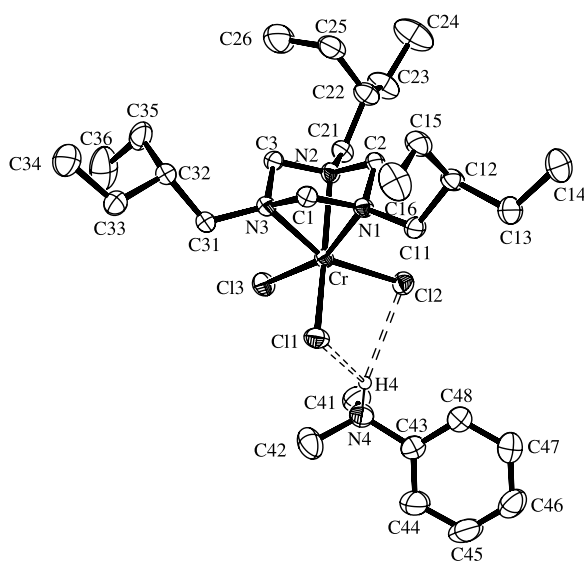
Fig. 1. Structure of **1a** (disorder in one substituent not shown).

Observation of the NMR spectra after addition of the aluminium alkyl leads to the reappearance of narrow aniline signals and disappearance of the *m*-F and severe broadening of the *o*- and *p*-F signals. This is also maintained after addition of 1-hexene and during catalysis. Thus the anion fills a free coordination site in the resting state of the activated catalyst (Scheme 3). The observation of only no more than three  $^{19}\text{F}$ -NMR signals in **2** and **3** indicates that fast exchange between all *o*-, *m*- and *p*-F positions occurs on the NMR time scale at ambient conditions leading to average linewidths.

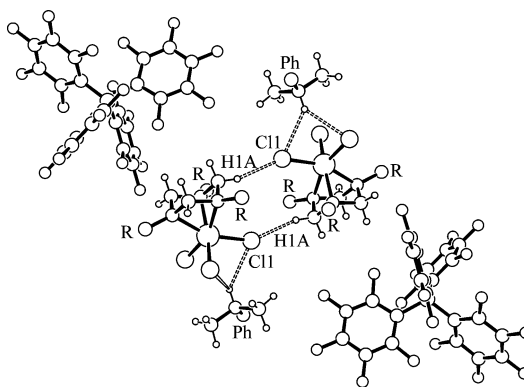
Initially, the linewidths of the *ortho*- and *para*- $^{19}\text{F}$ -NMR signals are similar before and after addition of 1-

hexene indicating a similar anion coordination. However, the decomposition of the active chromium complex leads to a sharpening of the  $^{19}\text{F}$ -NMR signals. This process occurs within days without added 1-hexene and within hours in the presence of 1-hexene. The *meta*-F signal becomes detectable after 1 week (1 day in the presence of 1-hexene) and yellow crystals separate from the solution that analyse as  $[(\text{arene})_2\text{Cr}][\text{B}(\text{C}_6\text{F}_5)_4]$  (arene = benzene **3A** or toluene **3B** depending on the solvent used). In repeated runs 10–20% of the chromium were isolated in these crystals. The crystal structures of  $\text{d}_{12}$ -**3A** and **3B** are shown in Fig. 4. The Cr–C bond distances (2.13–2.16 Å for  $\text{d}_{12}$ -**3A** and 2.10–2.18 Å for **3B**) are similar to those found for the cations in other  $[(\text{arene})_2\text{Cr}]^+$  salts [28]. **3B** has a disordered cation with the major component having nearly eclipsed methyl groups. This unusual conformation is probably due to crystal packing.

The observation of **3** proves that the oxidation state +I can be reached in the system and supports the proposed mechanism via Cr(I).  $[(\text{Arene})_2\text{Cr}]^+$  has previously been observed to about 0.4% in a mixture of  $\text{Cr}(\text{acac})_3$  and  $\text{AlEt}_3$  by ESR [29]. The much larger amount of Cr(I) isolated in our system suggests that the triazacyclohexane ligand may be involved in its formation. Close inspection of the  $^1\text{H}$ -NMR spectra of the catalytic system after substantial decomposition shows the appearance of two doublets in the region of 3–4

Fig. 2. Structure of cation in **2a** and a simplified plot of the neighbouring ions.Fig. 3. Structure of the cation in **2b**.

ppm. The chemical shifts are different for different *N*-substituents (**4b,c**). Similar doublets have previously been observed for the two types of ring hydrogen atoms in triazacyclohexanes coordinated in  $\kappa^3$  fashion to diamagnetic metal centres [30]. As Al(III) is the only diamagnetic metal in the system, an aluminium complex must have been formed.  $\text{Al}^i\text{Bu}_3$  does not react with  $\text{R}_3\text{TAC}$  to form  $\kappa^3$  complexes. However, when one equivalent of DMAB is added, the previously observed doublet pattern at nearly identical shifts confirm the formation of  $[(\text{R}_3\text{TAC})\text{Al}^i\text{Bu}_2][\text{B}(\text{C}_6\text{F}_5)_4]$  **4b,c**. The anion in the diamagnetic environment of **4** is in fast exchange with the anions in remaining **3** resulting in narrowing average linewidths for the  $^{19}\text{F}$ -NMR signals with proceeding decomposition. Comparison of the integrals for the aniline (one equivalent per chromium) and the aluminium complex shows that at least 50% of the original triazacyclohexane is transferred from the

Table 1  
Selected bond distances (Å) and angles (°)

|                         | <b>1a</b>   | <b>2a</b>         | <b>2b</b>         |
|-------------------------|-------------|-------------------|-------------------|
| Cr–N1                   | 2.0974(18)  | 2.1162(14)        | 2.1028(18)        |
| Cr–N2                   | 2.1015(19)  | 2.0826(14)        | 2.1150(19)        |
| Cr–N3                   | 2.1087(16)  | 2.0983(14)        | 2.0951(19)        |
| av. Cr–N                | 2.103(6)    | 2.099(17)         | 2.104(10)         |
| Cr–Cl1                  | 2.2853(6)   | 2.2956(5)         | 2.2928(7)         |
| Cr–Cl2                  | 2.2791(6)   | 2.2696(5)         | 2.2826(7)         |
| Cr–Cl3                  | 2.2658(7)   | 2.2918(5)         | 2.2818(6)         |
| av. Cr–Cl               | 2.277(10)   | 2.286(14)         | 2.286(6)          |
| Cl1–H4                  |             | 2.65 <sup>a</sup> | 2.74 <sup>a</sup> |
| Cl2/3–H4                |             | 2.60 <sup>a</sup> | 2.59 <sup>a</sup> |
| av. N–Cr–N              | 66.2(5)     | 66.15(10)         | 66.2(2)           |
| Cl1–Cr–Cl2              | 97.84(3)    | 99.901(19)        | 97.43(3)          |
| Cl1–Cr–Cl3              | 99.63(3)    | 95.865(18)        | 98.38(2)          |
| Cl2–Cr–Cl3              | 99.60(3)    | 99.697(19)        | 98.03(3)          |
| av. Cl–Cr–Cl            | 99.0(1.0)   | 98.5(2.3)         | 97.9(5)           |
| av. Cr–N–C <sub>R</sub> | 127.7(11.7) | 126.2(2.4)        | 125.3(2.0)        |

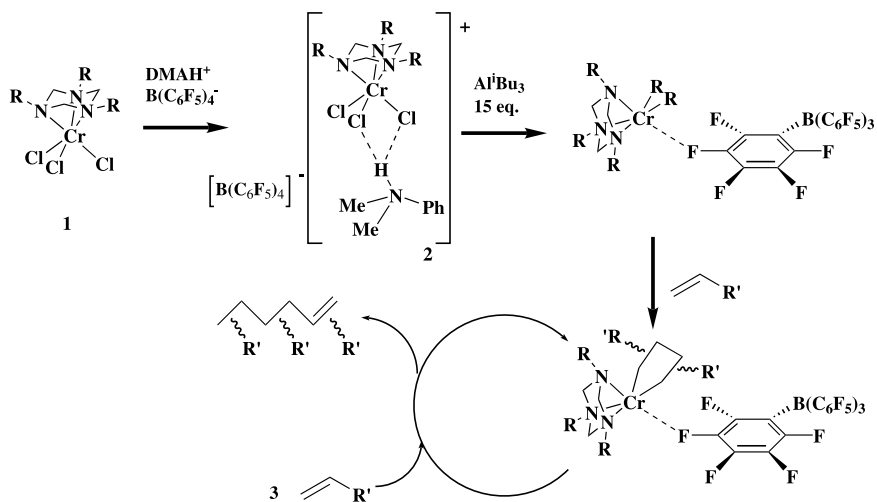
<sup>a</sup> Distances to hydrogens are based on the calculated positions in the refinement.

chromium to aluminium. An approximate stoichiometry of the decomposition that agrees with the observed intensities is given in Scheme 4.

Transfer of the triazacyclohexane ligands from chromium to aluminium on the Cr(I) stage of the proposed cycle would lead directly to **3**. However, some of the triazacyclohexane must remain coordinated to an inactive possibly multinuclear chromium(III) complex to account for the previously observed new paramagnetically shifted signals for coordinated ligand. We are currently investigating the exact stoichiometry of the decomposition and the nature of the other products.

### 3. Conclusion

Activation of  $[(\text{triazacyclohexane})\text{CrCl}_3]$  with DMAB and  $\text{Al}^i\text{Bu}_3$  leads to an active complex with similar

Scheme 3. Activation with DMAB/ $Al^i Bu_3$ .

catalytic olefin trimerisation activity as activation with MAO. However, the well defined borate anion permits isolation and crystallographic characterisation of hydrogen bonded anilinium adducts to the chromium chloride complex during activation, and bis(arene) chromium(I) complexes as catalyst decomposition products. This observation shows that reduction to Cr(I) can occur in this system. During catalysis itself, a cationic Cr(III) complex with the weakly coordinating borate anion occupying one coordination site is found to be the resting state as shown by  $^{19}F$ -NMR.

#### 4. Experimental

All manipulations were carried out under nitrogen on a standard vacuum line, argon in a Saffron glove box,

and using Schlenk techniques. Solvents were dried according to standard methods.  $CrCl_3(THF)_3$  was purchased from Aldrich.  $^1H$ -,  $^{13}C\{^1H\}$ - and  $^{19}F$ -NMR spectra were recorded on a Bruker 300 or Varian 400 instrument.  $[(n-Do_3TAC)CrCl_3]$  was prepared as described previously [24].

#### 4.1. Synthesis of $(PhCH_2CH_2)_3TAC$ [31]

$(PhCH_2CH_2)_3TAC$  was prepared analogously to  $(Et_2CHCH_2)_3TAC$  and repeatedly recrystallised from hexane until a colourless solid was obtained in 62% yield. M.p.  $38^\circ C$ ;  $^1H$ -NMR (400 MHz):  $\delta(CDCl_3)$  7.38 (6H, m, *m-Ph*), 7.29 (9H, m, *o, p-Ph*), 3.52 (6H, br, N- $CH_2$ -N), 2.83 (12H, m, N- $CH_2CH_2Ph$ ).  $^{13}C$ -NMR (75 MHz):  $\delta(CDCl_3)$  140.1 (*i-Ph*), 128.5, 128.1 (m, *o-Ph*),

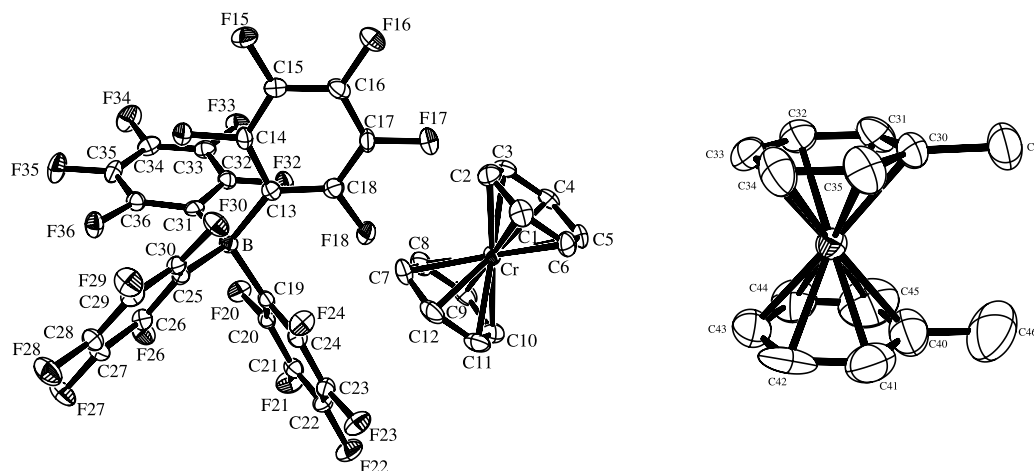
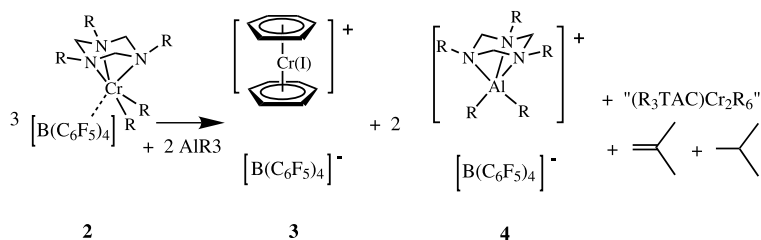


Fig. 4. Structure of the ions in **3A** (left) and of the cation in the analogous **3B** (right). Average Cr–C bond distance in angstrom: 2.14 (**3A**) and 2.15 (**3B**).



Scheme 4. Proposed stoichiometry of the decomposition reaction ( $R = \text{Et}_2\text{CHCH}_2$  (**2b**) and  $R = n$ -dodecyl (**2c**), arene solvent is  $\text{C}_6\text{D}_6$  for **3A** and toluene for (**3B**).

125.7 ( $p$ -Ph), 74.2 (N- $\text{CH}_2$ -N), 54.2 (N- $\text{CH}_2\text{CH}_2\text{Ph}$ ), 34.3 (N- $\text{CH}_2\text{CH}_2\text{Ph}$ ).

#### 4.2. Synthesis of $(\text{Et}_2\text{CHCH}_2)_3\text{TAC}$

2-Ethyl- $n$ -butylamine (2 g, 19.8 mmol) and paraformaldehyde (0.59 g, 19.8 mmol) were stirred in toluene (20 ml). After 4 h, half the toluene and the water produced during the reaction were removed by distillation. The remaining solvent was removed in vacuo, resulting in a colourless liquid of  $(\text{Et}_2\text{CHCH}_2)_3\text{TAC}$ . Yield, 1.8 g (80%).  $^1\text{H-NMR}$  (300 MHz):  $\delta(\text{CDCl}_3)$  3.26 (6H, br, N- $\text{CH}_2$ -N), 2.27 (6H, d,  $J_{\text{H,H}} = 5.3$  Hz, N- $\text{CH}_2$ -C), 1.32 (15H, m, C- $\text{CH}(\text{CH}_2)_2$ ), 0.85 (18H, t,  $J_{\text{H,H}} = 7.2$  Hz,  $\text{CH}_3$ ).  $^{13}\text{C-NMR}$  (75 MHz):  $\delta(\text{CDCl}_3)$  75.8 (N- $\text{CH}_2$ -N), 56.7 (N- $\text{CH}_2$ -C), 39.2 ( $\text{CH}(\text{CH}_2\text{CH}_3)_2$ ), 24.7 ( $\text{CH}(\text{CH}_2\text{CH}_3)_2$ ), 11.3 (C- $\text{CH}(\text{CH}_2\text{CH}_3)_2$ ).

#### 4.3. Synthesis of $[((\text{PhCH}_2\text{CH}_2)_3\text{TAC})\text{CrCl}_3]$ (**1a**)

$(\text{PhCH}_2\text{CH}_2)_3\text{TAC}$  (1.0 g, 2.5 mmol) and  $\text{CrCl}_3(\text{THF})_3$  (1.0 g, 2.7 mmol) were stirred in THF (20 ml) for 20 h. Addition of water, filtration, repeated washings with first water and then  $\text{Et}_2\text{O}$  and drying in vacuo resulted in a purple solid of  $[((\text{PhCH}_2\text{CH}_2)_3\text{TAC})\text{CrCl}_3]$ . Yield, 1.3 g (93%), m.p. 285 °C (dec.). Anal. Calc. for  $\text{C}_{27}\text{H}_{33}\text{Cl}_3\text{CrN}_3$  (557.93): C, 58.12; H, 5.96; Cr 9.32; N, 7.53. Found: C, 57.92; H, 6.20; Cr 9.45; N, 7.87%. Solubility was too low for NMR.

#### 4.4. Synthesis of $[((\text{Et}_2\text{CHCH}_2)_3\text{TAC})\text{CrCl}_3]$ (**1b**)

$(\text{Et}_2\text{CHCH}_2)_3\text{TAC}$  (1 g, 2.9 mmol) and  $\text{CrCl}_3(\text{THF})_3$  (1.103 g, 2.9 mmol) were stirred in THF (30 ml) for 12 h. Filtration, repeated washings with  $\text{Et}_2\text{O}$  then drying in vacuo resulted in a purple solid of  $[((\text{Et}_2\text{CHCH}_2)_3\text{TAC})\text{CrCl}_3]$ . Yield, 0.82 g (56%), m.p. 234 °C (dec.). Anal. Calc. for  $\text{C}_{21}\text{H}_{45}\text{N}_3\text{CrCl}_3$  (497.96): C, 50.65; H, 9.11; N, 8.44. Found: C, 50.10; H, 9.03; N, 8.21%.  $^1\text{H-NMR}$  (400 MHz):  $\delta(\text{CDCl}_3/\text{DMSO})$  3.86 (6H, bs, N- $\text{CH}_2$ -N), 1.96 (6H, bs, N- $\text{CH}_2$ -C), 1.67 (3H, bs, C- $\text{CH}[\text{C}]_2$ ), 1.30 (12H, bs, C- $\text{CH}_2$ -C), 0.91

(18H, bs, C- $\text{CH}_3$ ).  $^{13}\text{C-NMR}$  (100 MHz):  $\delta(\text{CDCl}_3/\text{DMSO})$  39.22 (6C, bs, C- $\text{CH}_2$ -C), 12.98 (6C, bs, C- $\text{CH}_3$ ).

#### 4.5. Synthesis of $[((\text{PhCH}_2\text{CH}_2)_3\text{TAC})\text{CrCl}_3]$ [DMAB] (**2a**)

$[((\text{PhCH}_2\text{CH}_2)_3\text{TAC})\text{CrCl}_3]$  (0.1 g, 0.18 mmol) and DMAB (0.144 g, 0.18 mmol) were stirred in toluene (10 ml) for 10 min. This solution was layered with hexane (10 ml) and left to stand for 4 days. Filtration, repeated washings with hexane and drying in vacuo resulted in purple crystals of  $[((\text{PhCH}_2\text{CH}_2)_3\text{TAC})\text{CrCl}_3(\text{PhMe}_2\text{NH})][\text{B}(\text{C}_6\text{F}_5)_4]$ . Yield, 0.14 g (57%), m.p. 251 °C (dec.). Anal. Calc. for  $\text{C}_{48}\text{H}_{57}\text{BCl}_3\text{CrF}_{20}\text{N}_4$  (1366.09): C, 51.87; H, 3.32; N, 4.10. Found: C, 52.60; H, 3.37; N, 4.21%.  $^{19}\text{F-NMR}$  (376 MHz):  $\delta(\text{CDCl}_3)$  -130.48 (8F, bs,  $o$ -ArF), -159.95 (4F, bs,  $p$ -ArF), -163.30 (8F, bs,  $m$ -ArF).

#### 4.6. Synthesis of $[((\text{Et}_2\text{CHCH}_2)_3\text{TAC})\text{CrCl}_3]$ [DMAB] (**2b**)

$[((\text{Et}_2\text{CHCH}_2)_3\text{TAC})\text{CrCl}_3]$  (0.1 g, 0.2 mmol) and DMAB (0.161 g, 0.2 mmol) were stirred in toluene (10 ml) for 10 min. This solution was layered with hexane (10 ml) and left to stand for 4 days. Filtration, repeated washings with hexane then drying in vacuo resulted in purple crystals of  $[((\text{Et}_2\text{CHCH}_2)_3\text{TAC})\text{CrCl}_3(\text{PhMe}_2\text{NH})][\text{B}(\text{C}_6\text{F}_5)_4]$ . Yield, 0.19 g (71%), m.p. 234 °C (dec.). Anal. Calc. for  $\text{C}_{53}\text{H}_{57}\text{BCl}_3\text{CrF}_{20}\text{N}_4$  (1299.18): C, 49.00; H, 4.42; N, 4.31. Found: C, 49.90; H, 4.34; N, 4.02%.  $^1\text{H-NMR}$  (400 MHz):  $\delta(\text{C}_6\text{D}_6)$  1.312 (12H, br, C- $\text{CH}_2$ -C), 0.933 (18H, br, C- $\text{CH}_3$ ).  $^{13}\text{C-NMR}$  (100 MHz):  $\delta(\text{C}_6\text{D}_6)$  36.67 (6C, br, C- $\text{CH}_2$ -C), 12.00 (6C, br, C- $\text{CH}_3$ ).  $^{19}\text{F-NMR}$  (376 MHz):  $\delta(\text{C}_6\text{D}_6)$  -132 (8F,  $\Delta\nu_{1/2}$  150 Hz,  $o$ -ArF), -162 (4F,  $\Delta\nu_{1/2}$  90 Hz,  $p$ -ArF), -165 (8F,  $\Delta\nu_{1/2}$  145 Hz,  $m$ -ArF).

#### 4.7. Synthesis of $[(\text{C}_7\text{H}_8)_2\text{Cr}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**3B**)

$[(n\text{-Do}_3\text{TAC})\text{CrCl}_3]$  (0.4 g, 0.5 mmol) and DMAB (0.426 g, 0.5 mmol) were stirred in toluene (5 ml) for 5

min. To this solution was added  $Al^iBu_3$  as 1.0 M solution in hexane (2.5 g, 3.6 mmol). The resulting green solution was left to stand at  $-14^\circ C$  for 3 days upon which yellow crystals of  $[(C_7H_8)_2Cr] [B(C_6F_5)_4]$  were formed. Yield, 0.06 g (12%). Anal. Calc. for  $C_{38}H_{16}BCrF_{20}$  (922.25): C, 49.86; H, 1.76; N, 0.0. Found: C, 49.90; H, 2.10; N, 0.12%.

4.8. NMR-tube reaction of  $[(Et_2CHCH_2)_3TAC)CrCl_3] [DMAB] (2b)$  with  $Al^iBu_3/1$ -hexene

$[(Et_2CHCH_2)_3TAC)CrCl_3] [DMAB]$  (1.4 mg, 0.0011 mmol) were dissolved in  $C_6D_6$  (1 ml) and 43  $\mu l$   $Al^iBu_3$  as 1.0 M solution in hexane (0.044 mmol) was added. NMR of the resulting green solution 10 min after the addition showed in the  $^1H$ -NMR isobutylene (4.8 ppm) and DMA (7.0, 6.9 and 2.3 ppm) and in the  $^{19}F$ -NMR (376 MHz):  $\delta(C_6D_6) -132$  (8F,  $\Delta\nu_{1/2}$  207 Hz, *o*-ArF),  $-160$  (8F,  $\Delta\nu_{1/2}$  2000 Hz, *m*-ArF),  $-162$  (4F,  $\Delta\nu_{1/2}$  90 Hz, *p*-ArF). 1-Hexene (20 mg, 0.24 mmol) was added and left to trimerise and decompose for 1 day. A mixture of hexene trimers [24] has formed with 75% conversion and yellow crystals have separated from the solution.

$^1H$ -NMR of the solution also shows two small doublets at 3.60 and 3.05 ppm ( $J=9$  Hz, ring  $CH_2$  of the aluminium complex).

4.9. NMR-tube reaction of  $[(n-Do_3TAC)CrCl_3] (1c)$  with DMAB,  $Al^iBu_3$  and 1-hexene and crystallisation of 3A

$[(n-Do_3TAC)CrCl_3]$  (6 mg, 0.008 mmol) and DMAB (9 mg, 0.011 mmol) were dissolved in  $C_6D_6$  (1 ml).  $^{19}F$ -NMR (376 MHz):  $\delta(C_6D_6) -132$  (8F,  $\Delta\nu_{1/2}$  225 Hz, *o*-ArF),  $-162$  (4F,  $\Delta\nu_{1/2}$  155 Hz, *p*-ArF),  $-165$  (8F,  $\Delta\nu_{1/2}$  231 Hz, *m*-ArF). To this solution was added 55  $\mu l$   $Al^iBu_3$  as 1.0 M solution in hexane (0.055 mmol) and 27 mg 1-hexene (0.32 mmol). NMR of the resulting green solution 10 min after the addition showed 1-hexene in the  $^1H$ -NMR (5.9 and 5.1 ppm) and  $^{19}F$ -NMR (376 MHz):  $\delta(C_6D_6) -130$  (8F,  $\Delta\nu_{1/2}$  540 Hz, *o*-ArF),  $-158$  (4F,  $\Delta\nu_{1/2}$  870 Hz, *p*-ArF). After 2 days a mixture of hexene trimers [24] has formed with 60% conversion by integration of the olefinic region and yellow crystals of 3A have separated from the solution. Anal. Calc. for  $C_{36}D_{12}BCrF_{20}$  (899.33): C, 48.08; H, 1.34 [32]; N, 0.0. Found: C, 48.50; H, 1.58; N, 0.22%.  $^1H$ -NMR of the

Table 2  
Summary of crystallographic data for compounds 1a, 2a, 2b, 3A and 3B

| Compound   | 1a   | 2a  | 2b*(toluene) <sub>0.5</sub>   | 3A*(C <sub>6</sub> D <sub>6</sub> ) <sub>0.5</sub> | 3B*(toluene) <sub>0.5</sub>                            |
|--|--|---|---|--|--|
| Empirical formula  | C <sub>27</sub> H <sub>33</sub> Cl <sub>3</sub> CrN <sub>3</sub> | C <sub>59</sub> H <sub>45</sub> BCl <sub>3</sub> CrF <sub>20</sub> N <sub>4</sub> | C <sub>56.5</sub> H <sub>60.5</sub> BCl <sub>3</sub> CrF <sub>20</sub> N <sub>4</sub> | C <sub>39</sub> H <sub>15</sub> BCrF <sub>20</sub> | C <sub>41.5</sub> H <sub>19.5</sub> BCrF <sub>20</sub> |
| <i>M</i> (g mol <sup>-1</sup> )  | 557.91   | 1359.15   | 1344.75   | 926.32   | 960.88   |
| Crystal colour   | Purple   | Purple  | Purple  | Yellow   | Yellow   |
| Crystal size (mm)  | 0.5 × 0.15 × 0.08  | 0.38 × 0.25 × 0.10  | 0.5 × 0.4 × 0.15  | 0.38 × 0.13 × 0.03                                 | 0.3 × 0.25 × 0.13                                      |
| Crystal system   | Monoclinic   | Triclinic   | Monoclinic  | Triclinic  | Monoclinic   |
| Space group  | <i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)                      | <i>P</i> $\bar{1}$ (no. 2)  | <i>P</i> 2 <sub>1</sub> / <i>n</i> (no. 14)   | <i>P</i> $\bar{1}$ (no. 2)                         | <i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)            |
| <i>a</i> (Å)   | 11.6360(2)   | 13.4030(2)  | 12.3190(1)  | 8.1330(2)  | 10.4850(2)   |
| <i>b</i> (Å)   | 17.1910(3)   | 15.0830(2)  | 30.5470(3)  | 13.3590(3)   | 21.8690(4)   |
| <i>c</i> (Å)   | 14.0810(3)   | 15.2570(2)  | 16.5740(2)  | 16.2770(4)   | 16.8810(4)   |
| $\alpha$ (°)   |  | 63.8900(6)  |   | 107.1960(11)                                       |  |
| $\beta$ (°)  | 109.784(1)   | 82.3890(6)  | 107.870(10)   | 97.2240(11)  | 103.971(1)   |
| $\gamma$ (°)   |  | 80.4760(6)  |   | 93.3740(13)  |  |
| <i>V</i> (Å <sup>3</sup> )   | 2650.43(9)   | 2903.81(7)  | 5936.14(10)   | 1667.39(7)   | 3756.25(13)  |
| <i>Z</i>   | 4  | 2   | 4   | 2  | 4  |
| <i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )                         | 1.398  | 1.554   | 1.505   | 1.845  | 1.699  |
| $\mu$ (Mo–K $\alpha$ ) (mm <sup>-1</sup> )                             | 0.755  | 0.443   | 0.432   | 0.489  | 0.437  |
| 2 $\theta$ Range (°)   | 8–55   | 7–55  | 6–54  | 6–55   | 7–55   |
| Collected data   | 45 752   | 41 201  | 41 284  | 25 661   | 27 245   |
| Unique Data ( <i>I</i> > 2 $\sigma$ <i>I</i> )                         | 6064 ( <i>R</i> <sub>int</sub> = 0.074)                          | 13 271 ( <i>R</i> <sub>int</sub> = 0.041)   | 12 904 ( <i>R</i> <sub>int</sub> = 0.063)   | 7625 ( <i>R</i> <sub>int</sub> = 0.079)            | 8310 ( <i>R</i> <sub>int</sub> = 0.074)                |
| Refined parameter  | 321  | 793   | 775   | 550  | 660  |
| Min/max density (e Å <sup>-3</sup> )                                   | –0.504/0.378   | –0.487/0.271  | –0.677/0.456  | –0.585/0.303                                       | –0.475/0.299   |
| Extinction coefficient <sup>a</sup>                                    | 0.0054(7)  |   |   |  |  |
| <i>R</i> <sub>1</sub> <sup>b</sup> ( <i>I</i> > 2 $\sigma$ <i>I</i> )  | 0.0396   | 0.0358  | 0.0441  | 0.0443   | 0.516  |
| <i>wR</i> <sub>2</sub> <sup>c</sup> ( <i>I</i> > 2 $\sigma$ <i>I</i> ) | 0.0865   | 0.0857  | 0.0984  | 0.0905   | 0.1138   |
| Goodness-of-fit <sup>d</sup>   | 1.019  | 1.022   | 1.015   | 1.020  | 1.011  |

<sup>a</sup>  $F_c = kF_c[1 + 0.001F_c^2\lambda^3/\sin(2\theta)]^{-1/4}$ .

<sup>b</sup>  $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ .

<sup>c</sup>  $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ .

<sup>d</sup>  $GOF = S = \{\Sigma[w(F_o^2 - F_c^2)^2/(n-p)]\}^{1/2}$ .

solution also shows two small doublets at 3.48 and 2.93 ppm (ring CH<sub>2</sub> of the aluminium complex).

#### 4.10. NMR-tube synthesis of

$[(Et_2CHCH_2)_3TAC)Al^iBu_2][B(C_6F_5)_4]$  (**4b**)

(Et<sub>2</sub>CHCH<sub>2</sub>)<sub>3</sub>TAC (0.032 g, 0.094 mmol), DMAB (0.075 g, 0.094 mmol), and Al<sup>i</sup>Bu<sub>3</sub> as 1.0 M solution in hexane (0.29 g, 0.29 mmol) were dissolved in benzene-*d*<sub>6</sub> (1 ml) to form a colourless solution of  $[(Et_2CHCH_2)_3TAC)Al^iBu_2][B(C_6F_5)_4]$  **4b**. <sup>1</sup>H-NMR (300 MHz): δ(C<sub>6</sub>D<sub>6</sub>) 3.73 (3H, d, *J*<sub>Ha,Hb</sub> = 8.9 Hz, N-CH<sub>a</sub>H<sub>b</sub>-N), 3.08 (3H, d, *J*<sub>Hb,Ha</sub> = 8.9 Hz, N-CH<sub>b</sub>H<sub>a</sub>-N), 1.70 (2H, m, C-CH-C), 0.92 (12H, d, *J*<sub>H,H</sub> = 6.4 Hz, C-CH<sub>3</sub>), 0.24 (4H, d, *J*<sub>H,H</sub> = 7.0 Hz, Al-CH<sub>2</sub>-C).

#### 4.11. NMR-tube synthesis of $[(n-Do_3TAC)Al^iBu_2]$

$[B(C_6F_5)_4]$  (**4c**)

Do<sub>3</sub>TAC (0.022 g, 0.037 mmol), DMAB (0.03 g, 0.037 mmol), and Al<sup>i</sup>Bu<sub>3</sub> as 1.0 M solution in hexane (0.083 g, 0.12 mmol) were dissolved in benzene-*d*<sub>6</sub> (1 ml) to form a colourless solution of  $[(n-Do_3TAC)Al^iBu_2][B(C_6F_5)_4]$  (**4c**). <sup>1</sup>H-NMR (300 MHz): δ(C<sub>6</sub>D<sub>6</sub>) 3.48 (3H, d, *J*<sub>Ha,Hb</sub> = 8.9 Hz, N-CH<sub>a</sub>H<sub>b</sub>-N), 2.88 (3H, d, *J*<sub>Hb,Ha</sub> = 8.9 Hz, N-CH<sub>b</sub>H<sub>a</sub>-N), 1.76 (2H, m, C-CH-C), 0.95 (12H, d, *J*<sub>H,H</sub> = 6.3 Hz, C-CH<sub>3</sub>), 0.07 (4H, d, *J*<sub>H,H</sub> = 8.0 Hz, Al-CH<sub>2</sub>-C).

### 5. X-ray crystal structure determinations

Intensity data were collected at 150 K on a Nonius Kappa CCD equipped with a low temperature device, using graphite monochromated Mo-K<sub>α</sub> radiation (λ = 0.71070 Å) and processed using the NONIUS software [33]. For structure solution and refinement the programs SIR-97 [34] and SHELXL-97/2 [35] were used while illustrations were generated using ORTEP-3 [36]. Crystal parameters and details of the data collection, solution and refinement are summarised in Table 2. ORTEP graphics of the complexes are presented in Figs. 1–4, and selected bond lengths and angles in Table 1.

*Notes on the refinement:* In **1a** one of the ligand groups shows disorder in a ratio of 1:1. Atoms C21–C28, C21A–C28A of this disordered group were refined isotropically. **2b** and **3B** crystallise with half molecule of toluene per asymmetric unit which is disordered about a centre of inversion. The cation in **3B** is disordered in a ratio of 2:1 and Fig. 4 shows its major component. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 206260 for **1a**, 206258 for **2a**, 206259 for **2b**, 206262 for **3A** and 206262 for **3B**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2

1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>)

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