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Crystallographic Revelation of the Role of $AlMe_3$ (in MAO) in Cr [NNN] Pyrazolyl Catalyzed Ethylene Trimerization

Jun Zhang,[†] Aifang Li,[‡] and T. S. Andy Hor*[,†]

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Kent Ridge, Singapore, and Department of Chemistry, College of Chemistry and Chemical Engineering, and the MOE Key Laboratory of Ananlytical Sciences, Xiamen University, People's Republic of China

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Summary: A series of Cr–Al intermetallic complexes, viz. $[(Pz'_3CH)_2Cr^{II}_2(\mu\text{-}Cl)_2]_2^{+}\cdot 2[(Me_2XAl)(\mu\text{-}Cl)(Me_2XAl)]^{-}$ *(X = Me/Cl),* $Pz'_3CHCr^{III}MeCl(\mu\text{-}Cl)(AlMe_2X)$ *(X = Me/Cl), and* $Pz'_2CHCH_2(\mu\text{-}N)CH_2(\mu\text{-}Ph)Cr^{III}Cl(\mu\text{-}Cl)AlMe_2$*, have been isolated from the reactions of* $CrCl_3(NNN)$ *(NNN = tridentate pyrazolyl ligand) with neat* $AlMe_3$ *or commercial MAO solutions. The products generally show high activity and selectivity in ethylene trimerization. Crystallographic analysis has provided structural evidence for Cr(III) reduction by residual* $AlMe_3$ *in a mixture containing the "real" activator (MAO) as well as other transformations: viz., adduct formation, methylation, cationization, halide abstraction, N–H deprotonation, and C–H cleavage of an unactivated arene.*

The selective trimerization of ethylene has attracted vigorous attention recently, due largely to the importance of 1-hexene in the production of linear low-density polyethylene (LLDPE).[1] The trimerization mechanism is generally believed to involve metallacyclic intermediates,[2] but despite intensive studies, there remains considerable debate on the mechanistic details, such as the dynamics of the chromium oxidation states at different stages of the catalytic cycle.[1a,b] It has been proposed that the cocatalyst reduces the metal at the early stage of activation.[1a,b] One of the most commonly used trimerization cocatalysts is methylaluminoxane (MAO), the role of which is generally assumed to be metal alkylation followed by alkyl abstraction to give an ion pair.[1a] However, as the structural elucidation of the intermediates formed between the precatalytic Cr(III) and MAO remains a formidable challenge, the precise role of MAO in the trimerization pathway is still uncertain.[3] In the remarkable PNP (PNP = $Ph_2PN(R)PPh_2$) and Sasol SNS (SNS = $RSCH_2CH_2N(H)CH_2CH_2SR$) systems, several Al(III) activators (e.g., isobutylaluminoxane (^iBAO), $AlMe_3$, $AlEt_2Cl$, $AlMeCl_2$, and $AlCl_3$) are found to be active in the reduction,[4a,d] alkylation,[4a,b] chloride abstraction,[4a−d] cationization,[4b] and oxidation (or disproportionation) of the precatalysts.[4b] Attempts to probe the interaction between Cr(III) and the "real" cocatalyst MAO only resulted in "intractable materials".[4a] In the Sasol system, the N–H function in the SNS ligands is believed to be key to its performance, whereas the fairly acidic N–H bond is expected to be deprotonated in the process. Hence, the observed lack of reactivity of N–H toward Al(III) or Cr–R is perplexing.[4]

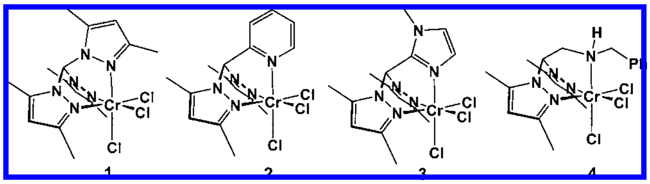

Figure 1. [NNN] pyrazolyl Cr(III) Complexes **1**–**4**.

We have recently isolated some unusual bi- and intermetallic intermediates that are catalytically relevant.[5] This was followed by the report of a highly selective trimerization Cr(III) catalytic system with heteroscorpionate pyrazolyl ligands of the type Pz'_2CHCH_2XR (Pz′ = 3,5-dimethylpyrazol-1-yl, X = O, S, R = alkyl, aryl).[6] These results prompted us to probe the activity of the actual activator MAO with precatalyst Cr(III) as a means to gain some structural insights into the mode of interaction. We herein choose model Cr(III) systems with [NNN] ligands of the type Pz'_2CHX (**1**–**4**; X = N-heterocycle or CH_2NHCH_2-Ph) (Figure 1) and their reaction with commercial MAO reagent that contains $AlMe_3$. Use of a similar tris(pyrazolyl)methane ligand with Cr(III) (i.e., **1**) as a highly selective trimerization catalyst has been patented.[7] X-ray single-crystal crystallographic analysis of the isolated materials revealed some intriguing intermetallic interactions and crystallographic evidence of the role of $AlMe_3$ (in MAO) in the reduction of the precatalyst. We also reveal the structural outcome of unexpected amine N–H deprotonation and arene C–H activation reactions on the bimetallic core.

The [NNN] pyrazolyl ligands were prepared by modified literature procedures.[8] Their treatment with $[CrCl_3(THF)_3]$ in THF afforded the corresponding Cr(III) complexes **1**–**4** in good yields (88–92%).

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* To whom correspondence should be addressed. Fax: (+65) 6873 1324. E-mail: andyhor@nus.edu.sg.

[†] National University of Singapore.

[‡] Xiamen University.

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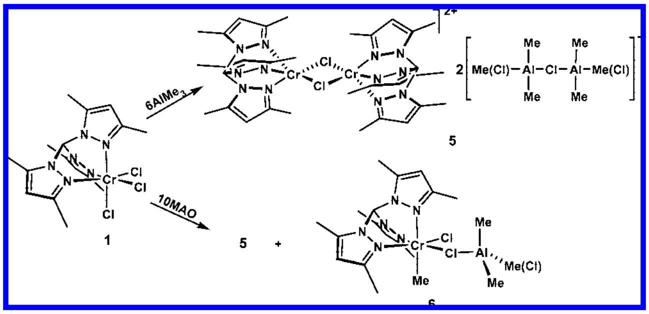
Table 1. Ethylene Trimerization Catalyzed by 1−7[a]

entry (complex)	amt of Cr (μmol)	PE (wt %)	C_6 (wt %)	C_8 (wt %)	C_{10} (wt %)	1-C_6 (wt %)	activity (g/((g of Cr) h))
1 (**1**)	8.7	<0.1	97.6	1.3	1.0	98.4	32 400
2 (**2**)	8.9	<0.1	97.8	1.1	1.0	99.3	38 200
3 (**3**)	7.9	<0.1	98.5	1.4	0	99.1	53 000
4 (**4**)	8.0	<0.5	92.1	3.5	3.9	98.7	10 500
5 (**5**)	5.5	<0.1	98.7	1.2	0	99.1	36 300
6 (**5**)[b]	6.1	<0.1	97.8	2.1	0	99.1	630
7 (**6**)	5.3	<0.1	97.8	1.1	1.0	99.3	37 400
8 (**7**)	8.9	<0.1	93.0	3.7	3.2	98.3	13 300

[a] Conditions: 200 MAO, 30 bar, 60 mL of toluene, 80 °C, 30 min. [b] $50 \cdot AlMe_3$.

Scheme 1. Reactions of 1 with $AlMe_3$ or Residual $AlMe_3$ in MAO



The catalytic performance of **1**−**4** toward ethylene trimerization is summarized in Table 1. At 80 °C under 30 bar of ethylene pressure and in the presence of MAO (Al:Cr = 200: 1), the precatalysts with a heterocycle group, i.e. a pyridinyl, imidazolyl, or pyrazolyl group, are highly selective toward trimerization (total C_6 selectivities >97.6%) to 1-hexene (>96.0%) with good activities of 32 400−53 000 g/((g of Cr) h) (entries 1−3). The highest activity is found in **3**, which has an imidazolyl group. Complex **4**, with an amino group, is less active and selective than those bearing a heterocyclic group (compare entry 4 with entries 1−3).

The reaction of **1** with 6 equiv of $AlMe_3$ results in a reduction to give cationic $[(Pz'_3CH)_2Cr_2(\mu\text{-}Cl)_2]^{2+} \cdot 2[(Me_2XAl)(\mu\text{-}Cl)(Me_2XAl)]^-$ (**5**; X = Me/Cl), isolated as green crystals in 79% yield (Scheme 1). It consists of a dinuclear chloride-bridged dication balanced by two dialuminate $[(Me_2XAl)_2(\mu\text{-}Cl)]^-$ anions. Each Me_2XAl moiety is crystallograhphically represented as a mix of $[Me_3Al]$ and $[Me_2ClAl]$.[9] The planar $[Cr^{II}_2Cl_2]$ rhombic core together with the supporting [NNN] ligands form an edge-sharing bi-square-pyramidal structure (Figure 2). Use of a 10 equiv excess of MAO gives the same product (61%) but also introduces the side product $Pz'_3CHCrMeCl(\mu\text{-}Cl)(AlMe_2X)$ (**6**; 9%) (Figure 3).[9] The latter is a product of methylation and Lewis adduct formation with $AlMe_3$, giving a single Cr−Cl−Al bridge. These reactions suggest that the residual $AlMe_3$ in commercial MAO solution (prepared from partial hydrolysis of $AlMe_3$) is an active ingredient in both metal reduction and M−Cl activation. When the MAO reagent was pretreated by removing $AlMe_3$ in vacuo at 50 °C for 5 h, neither **5** nor **6** was isolated in either reaction, suggesting that, in the early stage of activation, $AlMe_3$ is the active reductant in MAO. Complete removal of $AlMe_3$ was not successful in our hands. The isolation of **6** enables a rare glimpse of the possible mode of interaction between $AlMe_3$ and the Cr(III) species before reduction or ion formation takes place. The reaction of **6** and 2 equiv of $AlMe_3$ leads to the formation of **5** in 89% yield, suggesting that **5** is the reductive product of **6** by $AlMe_3$. In the

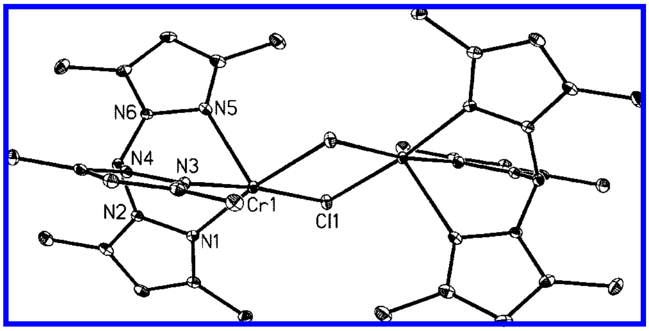


Figure 2. Molecular structure of **5**. The two $[(Me_2AlMe(Cl))_2(\mu\text{-}Cl)]^-$ counteranions in **5** are omitted for clarity. Selected bond lengths (Å) and angles (deg) for **5**: Cr1−N1 = 2.091(3), Cr1−N3 = 2.087(3), Cr1−N5 = 2.290(3), Cr1−Cl1 = 2.384(1), Cr1−Cl2 = 2.376(1); N3−Cr1−Cl1 = 173.27(9), N1−Cr1−Cl1 = 94.29(8), N(3)−Cr(1)−N(1) = 83.68(11), N(3)−Cr(1)−N(5) = 83.01(11), N(1)−Cr(1)−N(5) = 85.85(11), Cl2−Cr1−Cl1 = 85.52(3), Cr2−Cl1−Cr1 = 94.48(3).

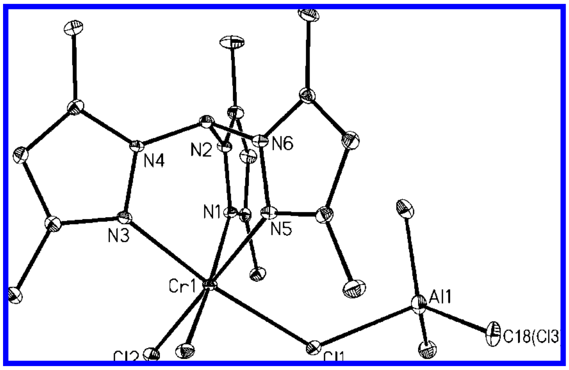


Figure 3. Molecular structure of **6**. The toluene solvate in **6** has been omitted for clarity. Selected bond lengths (Å) and angles (deg) for **6**: Cr1−N1 = 2.235(2), Cr1−N3 = 2.085(2), Cr−N5 = 2.094(2), Cr−Cl2 = 2.3213(7), Cr−Cl1 = 2.4182(7), Al−Cl1 = 2.346 (1); N(3)−Cr(1)−N(5) = 84.23(8), N(1)−Cr(1)−N(5) = 84.89(8), Cl2−Cr1−Cl1 = 89.09(3), Al−Cl(1)−Cr = 128.55(4).

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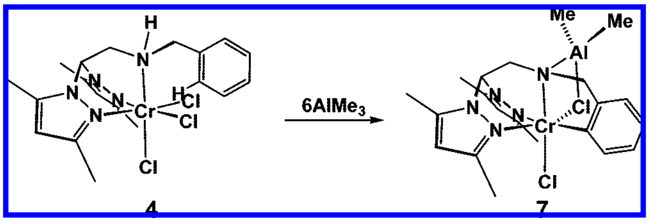
(9) The crystals were mounted on quartz fibers, and X-ray data were collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector at −50 °C, using Mo Kα radiation (λ = 0.710 73 Å). The data were corrected for Lorentz and polarization effects with the SMART suite of programs and for absorption effects with SADABS. Structure solution and refinement were carried out with the SHELXTL suite of programs. In complex **5**, each of the two $(Me_3Al)_2(\mu\text{-}Cl)$ counteranions has two of the six methyl group carbon atoms not properly behaving during the refinement. By arbitrarily attributing 13% chlorine character to one carbon atom, 22% chlorine character to another carbon atom, and the remaining as carbon character, respectively, it was possible to obtain a satisfactory refinement. Complex **6** has one molecule of toluene per chromium atom in the lattice, with one of the three methyl group (in $AlMe_3$) carbon atoms not properly behaving during the refinement. By arbitrarily attributing 33% chlorine character and the remaining as carbon character, it was possible to obtain a satisfactory refinement. The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms.

Scheme 2. Reaction of 4 with $AlMe_3$



Cr pyrrolyl ethylene trimerization system, Cr(III) ethyl hexanoate, $[Cr^{3+}(EH)_3]$, is proposed to be activated through one-electron inner shell reduction to $Cr^{2+}(EH)_2$ initiated by $AlEt_3$ and accompanied by ligand exchange and formation of ethyl radical.[10] Activated by MAO, both **5** and **6** show activities and selectivities similar to those of **1** (entries 1, 5, and 7 in Table 1), also suggesting that they could lead to similar catalytic species. Use of **5** with $AlMe_3$ as cocatalyst shows very low activity, indicating the indispensable role of MAO, especially in the late stages of the activation and trimerization process. $AlMe_3$ is believed to serve as the main reductant in the early stages of activation (compare entries 5 and 6).

C−H activation[11] is generally more common among heavy metals,[11b] partly because of the M−C and M−H bonds are stronger than for 3d metals such as Cr.[12] In the presence of a 6-fold excess of $AlMe_3$, complex **4** readily undergoes cyclometalation with C−H activation and a concomitant N−H cleavage to capture the Al moiety to give an unusual heterobimetallic Al−Cr complex, $Pz'_2CHCH_2(\mu\text{-N})CH_2(\mu\text{-Ph})CrCl(\mu\text{-Cl})AlMe_2$ (**7**) (Scheme 2 and Figure 4). The four-membered ring {Cr−N−Al−Cl} is possibly formed through a cycloheterometalation step via CH_4 elimination from a Cr−Cl−Al bridged adduct similar to that witnessed in **6**. Acid condensation would then explain the arene metalation. Similar intermolecular arene C−H activation has been reported in the reaction of $[N(o\text{-}C_6H_4P^iPr_2)_2]NiMe$ with benzene in the presence of $AlMe_3$, giving $[N(o\text{-}C_6H_4P^iPr_2)_2]NiPh$.[11b] Complexes **7** and **4** show similar trimerization activities (Table 1, entries 8 and 4).

It is remarkable that, within a single model system, there is crystallographic evidence of different functions of $AlMe_3$ as the catalyst activator: viz., adduct formation, methylation, reduction, cationization, halide abstraction, N−H deprotonation, and C−H cleavage of an unactivated arene. Among all the heterometallic species isolated, there is no spectroscopic or structural evidence of any MAO-stabilized adduct. Instead, the products conclusively point to an active and key reductive role of $AlMe_3$ in a trimerization process that contains the "real" coactivator: viz., MAO. Our study unveils some unexpected intermetallic-assisted ligand transformation, suggests that we may have underestimated the importance of adventitious $AlMe_3$ in MAO-activated ethylene oligomerization processes, and offers a possible reductive process for the Cr(III) precatalyst. The isolation of these catalytically relevant intermediates point to a complex and multifaceted role played by $AlMe_3$ (in MAO) in Cr−Al-catalyzed ethylene oligomerization processes, especially the reduction of precatalyst. It also offers a possible explanation of the complex and at times conflicting results of some related systems. While we are still far from deciphering the mechanistic details of the trimerization process, it is clear that interaction with the Al(III) activator with the commonly used tridentate ligand used in ethylene oligomerization cannot be ignored. Our next target is to probe the catalytic advantage of using multidentate ligands that can actively promote such interactions with the Al(III) activator and the stabilizing effect thus obtained from intermetal cooperativity in conjunction with C−H and N−H activations.

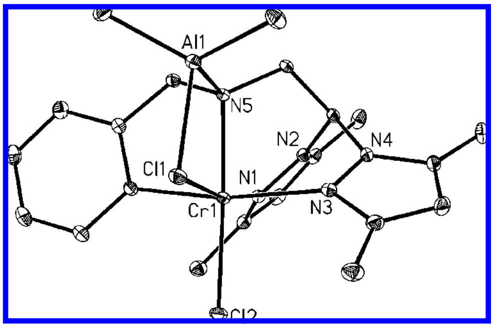


Figure 4. Molecular structure of **7**. Selected bond lengths (Å) and angles (deg) for **7**: Cr−C19 = 2.043(4), Cr−N1 = 2.058(3), Cr−N5 = 2.096(3), Cr−N3 = 2.186(3), Cr−Cl1 = 2.463(1), Al−N5 = 1.947(4), Al−Cl1 = 2.286(2); Al−N5−Cr = 100.5(1), Al−Cl1−Cr = 81.69(5), N5−Al−Cl1 = 93.1(1), C−Cr−N3 = 170.06(14), C−Cr−N5 = 82.86(14), C−Cr−Cl1 = 90.35(12).

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Supporting Information Available: Text and figures giving details of the syntheses and characterization data for all new compounds and CIF files giving X-ray crystallographic data for **5**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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