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Spectral Studies of a Cr(PNP)−MAO System for Selective Ethylene Trimerization Catalysis: Searching for the Active Species

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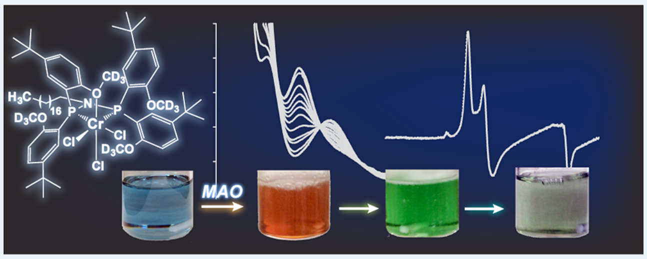
Ⓢ *Supporting Information*

ABSTRACT: Variable temperature spectroscopic, kinetic, and chemical studies were performed on a soluble $Cr^{III}Cl_3(PNP)$ (PNP = bis(diarylphosphino)alkylamine) ethylene trimerization precatalyst to map out its methylaluminoxane (MAO) activation sequence. These studies indicate that treatment of $Cr^{III}Cl_3(PNP)$ with MAO leads first to replacement of chlorides with alkyl groups, followed by alkyl abstraction, and then reduction to lower−valent species. Reactivity studies demonstrate that the majority of the chromium species detected are not catalytically active.

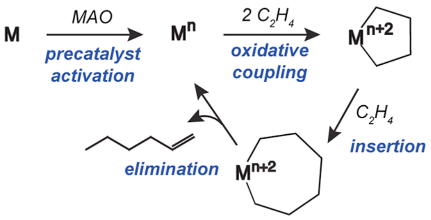


KEYWORDS: *chromium, ethylene trimerization, metallacycle, intermediates, methylaluminoxane, active species*

Development of selective oligomerization technologies to access α-olefins from inexpensive building blocks is an active area of petrochemical research.[1] The global demand for linear α-olefins alone is more than 4 million tons per year, primarily for the manufacture of chemical commodities such as polymers, detergents, and lubricants. Industrially, α-olefins are typically obtained from metal-catalyzed ethylene oligomerization that occurs via a Cossee-Arlman-type mechanism: sequential insertion of ethylene into metal−hydride or metal−alkyl species, followed by β-hydride elimination to afford a statistical distribution of α-olefins. In recent years, the discovery of metal-catalyzed transformations that can convert ethylene selectively to either 1-hexene or 1-octene has attracted considerable interest in the community.[2−4] Although a wide assortment of selective ethylene trimerization catalysts have now been reported, so far, only one has been commercialized, the Phillips Cr^{III}/2-ethylhexanoate/pyrrole/alkyl aluminum system.[2]

A mechanism that is generally proposed to account for this selectivity, involving metallacyclic intermediates formed by the oxidative coupling of two ethylenes followed by ring expansion (Scheme 1), has been experimentally confirmed by an isotopic labeling experiment.[5,6] However, there is very little definitive knowledge about the active catalytic species for any of these systems.[4] Work in our group[5−9] has focused on a class of catalysts generated from chromium(III) complexes of bis(diarylphosphino)alkylamine (PNP) ligands by activation with methylaluminoxane (MAO). Despite extensive experimental[5−8,10−14] and theoretical[15,16] studies of these systems, the nature of the active catalyst is still largely under debate, with unresolved questions regarding the oxidation state, the coordination geometry, and the ligand composition at the metal center.[4,17−23]

Scheme 1. Metallacycle Mechanism for Ethylene Trimerization



Characterization of these chromium species is particularly challenging because of their paramagnetism and the need for a large excess of MAO; application of techniques such as EPR and X-ray absorption (XAS) spectroscopies under catalytically relevant conditions have implicated both Cr^{I}/Cr^{III} [24] and Cr^{II}/Cr^{IV} [18,25] redox cycles. A fundamental ambiguity in such investigations, however, is the possibility that a very small amount of a highly active catalyst is responsible for most or all of the activity, whereas the species observed may take no part in the catalytic cycle—may not even be catalyst precursors—and hence, are essentially irrelevant to catalysis. In such a situation, which has been suggested as a possibility for metal-catalyzed olefin polymerization,[26−28] cycloisomerization,[29] 1,4-addition to enones,[30] and C−C bond cross-coupling,[31] it will be very difficult to establish any direct link between structure and activity. We report here observations that strongly indicate such is, indeed, the case for these Cr(PNP) systems.

We initially examined the precatalyst $Cr^{III}Cl_3(PN^{Me}P)$ (**1**, $PN^{Me}P$ = (bis(bis(2-methoxyphenyl)phosphino))methylamine, Chart 1),[7,13] using several spectroscopic techniques to follow its

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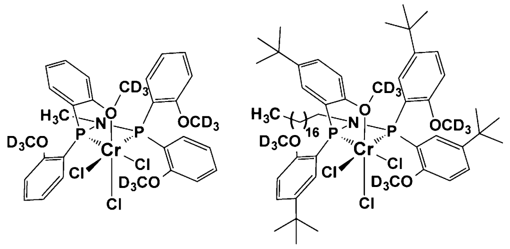
Chart 1. Structures of the Precatalysts 1 and 2



$Cr^{III}Cl_3(PN^{Me}P)$

1

$Cr^{III}Cl_3(PN^{C18}P)$

2

activation by MAO at low temperature, with the ultimate hope of identifying the active form of the chromium species by correlation with catalytic behavior under similar conditions. These studies were hampered by the limited solubility of **1**, so a more soluble form was generated by installing an octadecyl chain in the amine backbone and *tert*-butyl groups on the methoxyphenyl substituents of the PNP ligand. This ligand variant, $PN^{C18}P$, was prepared according to Scheme S1 (in the Supporting Information) and metalated with $Cr^{III}Cl_3(THF)_3$ to afford $Cr^{III}Cl_3(PN^{C18}P)$ (**2**, Chart 1).[32]

Upon addition of 500 equiv of MAO,[33] **2** exhibits ethylene trimerization catalysis very similar to **1** under 50 psi of ethylene in aromatic solvents (Table 1). 1-Hexene is the predominant product, along with small amounts of higher oligomers (mostly C_{10})[8] and polymer. Activity is favored by more-electron-deficient solvents: 1,2-difluorobenzene > chlorobenzene > toluene, a trend that has been noted previously in related systems.[25,34] No product is obtained in either dichloromethane or diethyl ether, possibly because of solvent coordination or rapid catalyst decomposition. Interestingly, activity with **2** is ~7 times higher than with **1** (entries 1 vs 2 in Table 1), which may reflect the improved solubility of **2**.

The reaction of MAO with **2** is accompanied by a sequence of color changes that can be followed by UV−visible (UV−vis) absorption spectroscopy.[35] Treatment of **2** in chlorobenzene with MAO at −40 °C results in an instantaneous color change from blue (λ_{max} = 500, 660 nm) to red (λ_{max} = 540 nm) (Figure 1A). The color further changes to green (λ_{max} = 448, 630 nm) over about an hour at −40 °C (Figure 1B); this conversion exhibits an isosbestic point at 602 nm and is first-order in chromium from a single wavelength kinetic analysis (Supporting Information Figure S2). The green color is relatively stable at −40 °C over the course of several hours. When **2** and MAO are mixed at 25 °C, no red color is observed (it would be expected to decay rapidly at this temperature); instead, the species corresponding to the green color forms directly and then gradually changes to a light blue-green color over the course of an hour. This transformation appears to take place in stages rather than being a simple conversion of one species to another: the spectra exhibit an isosbestic point only during the first phase (Figure 1C), and the data could not be fit to any simple kinetic function (Supporting Information Figure S3), suggesting that the blue-green color corresponds to at least two distinct species. ^2H NMR spectra recorded at −40 °C show significantly broadened peaks (Supporting Information Figure S4), consistent with paramagnetic species (see below).

Additional information on the sequence of formation of species was obtained from EPR spectroscopy. A solution of **2** in chlorobenzene frozen at −196 °C exhibits a broad rhombic signal, with *g* values at ~1.99, 3.02, and 4.57 (Figure 2A), consistent with other chromium(III) (S = 3/2) complexes.[36] When **2** is treated with MAO at −40 °C and immediately frozen, a new signal is observed, with g = 1.98, 3.50, and 4.34 (Figure 2B), characteristic for octahedral Cr^{III} with a large zero-field splitting and small rhombicity, E.[24,37] This spectrum closely resembles that reported for Cr^{III}/2-ethylhexanoate/alkyl aluminum,[24] suggesting that the chlorides in **2** have been replaced by alkyl groups from MAO to give $Cr^{III}R_3(PN^{C18}P)$ (**3**, where R = either methyl or butyl[33] groups from the MAO reagent). Double integration, using **2** as a spin standard, indicates that the conversion of **2** to **3** is nearly quantitative.

When the solution of **3** is allowed to stand at −40 °C, several new EPR signals (Figures 2C and Supporting Information S5) grow in, over roughly the same time span as the color change from red to green (see above). The major signal, which integrates as ~98% of the total amount of chromium (Cr_{total}), is characteristic of high-spin Cr^{III} (S = 3/2), with g = 3.85, 4.17, and 4.50. We tentatively assign this signal to the cationic complex $[Cr^{III}R_2(PN^{C18}P)]^+$ (**4**),[38] obtained from abstraction of an alkyl group from **3** by MAO.[16] Such a transformation would be consistent with the reaction being first-order in chromium. The minor component initially appears as a rhombic signal with g = 1.98, 2.00, and 2.03, characteristic of low-spin Cr^I (S = 1/2, designated as **5**), and integrating at only ~2% of Cr_{total}. Over time, another S = 1/2 signal grows in, similar to but clearly distinct from the first (Supporting Information Figure S5B), representing <1% of Cr_{Total}.

Finally, the reaction of **2** with MAO at 25 °C leads, after ~1 h, to yet another S = 1/2 signal (Figures 2D and Supporting Information S6), in this case axial (g = 1.98, 2.00). Such a signal has been shown to be characteristic of bis(arene)Cr^I sandwich complexes, which in the present case could be either $[Cr^I(\eta^6\text{-}C_6H_5Cl)_2]^+$ [39] or $[Cr^I(\text{bis-}\eta^6\text{-}PN^{C18}P)]^+$.[40,41] However, this signal accounts for only ~6% of Cr_{total}; the remainder of the chromium in solution is EPR-silent. A similar situation has been reported for a related Cr-PNP (tetramerization) catalyst, in which the EPR-active Cr^I component comprised only a small

Table 1. Ethylene Trimerization Data

entry	cat.	activation method[a]	T (°C)	activity[e] (g trimers/g Cr/h)	1-hexene (wt %)	higher trimers (wt %)	PE[f] (g)
1	1	I[b]	25	220 ± 120	99	1	1.17
2	2	I[b]	25	1446 ± 76	90	10	0.82
3	2	I[b]	− 40	75 ± 1	78	22	0.10
4	2	II[c]	25	512 ± 49	95	5	0.75
5	2	III[d]	25	672 ± 260	95	5	0.30

[a] General reaction conditions: complex **2** (11.8 μmol) in 25 mL of PhCl, MAO (250 mg, ~500 equiv), ethylene (50 psi). [b] Method I: pressurize reactor with ethylene before adding MAO. [c] Method II: add MAO, wait 15 s, then pressurize reactor with ethylene. [d] Method III: add MAO, wait 15 h, then pressurize reactor with ethylene. [e] Determined from the average of two independent trials. [f] Polyethylene.

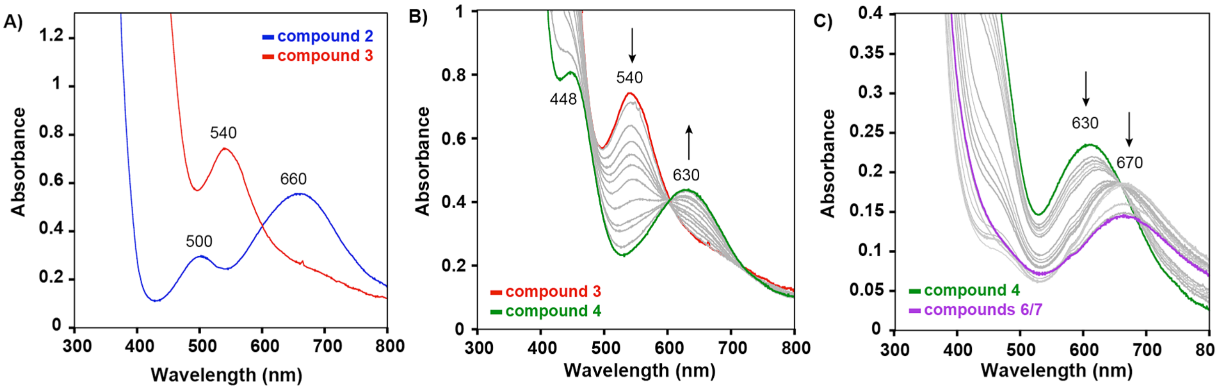


Figure 1. UV−vis absorption spectra obtained from addition of MAO to **2** (A, blue trace) immediately after mixing at −40 °C (A, red trace), reaction at −40 °C (B), and reaction at 25 °C (C). The concentration of the starting chromium complex is 946 μM. The traces are color-coded according to the species to which they are assigned: **2** (blue), **3** (red), **4** (green), **6**/**7** (purple).

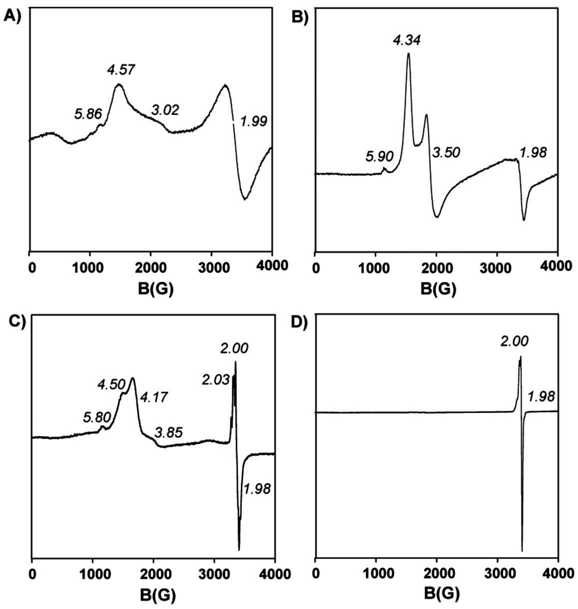
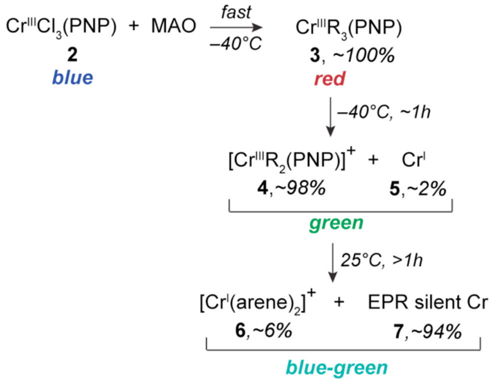


Figure 2. X-band EPR spectra of compound **2** in chlorobenzene (A) before addition of MAO, (B) immediately after mixing with MAO at −40 °C, (C) 1 h after mixing with MAO at −40 °C, and (D) 15 h after mixing with MAO at 25 °C. All spectra were recorded as frozen solutions at −196 °C; *g* values are given and also summarized in Supporting Information Table S2.

Scheme 2. Proposed Interpretation of Spectral Observations. 5 Is Most Likely Multiple Species



percentage of the total; the EPR-silent majority was suggested to be Cr^{II}, on the basis of XAS measurements,[18,25] although alternatives such as di- or polynuclear species are also possible.

The reaction sequence suggested by the combined UV−vis and EPR studies, along with proposed assignments (where possible), is summarized in Scheme 2. To assess possible participation of the observed intermediates in ethylene trimerization, catalytic trials were carried out under different conditions (Table 1). When an ethylene-saturated solution of **2** is cooled to −40 °C and then treated with MAO, a significant amount of catalytic trimerization can be observed after 1 h (entry 3), *even at such a low reaction temperature*. Under these conditions, the only spectrally observable species by EPR are **3**, **4**, and **5**. Additional reactions were conducted by pretreating **2** with MAO at 25 °C ~15 s (entry 4) and 15 h (entry 5) before introduction of ethylene. The spectral findings above indicate that no substantial amount of either **4** or **5** would be present in either case, whereas **3** would be present (but unstable) only in the first. The main component(s) in both of these cases would be the EPR-silent blue-green species **7**, along with a smaller amount of **6**, but neither appears to have formed under the conditions of entry 3. Nonetheless, *all* of these experiments exhibit good trimerization activity. The clear implication is that none of the major species observed by UV−vis or EPR—**3**, **4**, and **7**—is involved in catalysis.

Ruling out (or in) **5** or **6** as an active catalyst (or direct precursor thereto) is less clear-cut, as they are never present in more than small amounts. There is evidence that ethylene reacts with **5**: comparison of the EPR spectra obtained from the reaction of **2** with MAO at −40 °C in the presence and absence of ethylene reveals that the $S = 1/2$ signal attributed to **5** is suppressed in the former; there is a much weaker, similar but clearly different, signal that intensifies when the solution is allowed to warm to room temperature (Supporting Information Figure S7). In contrast, introduction of ethylene to a reaction mixture prepared at room temperature (blue-green) does not appear to result in any change in the EPR signal assigned to **6** (or the UV−vis spectrum that characterizes **7**).

To sum up: The preparation of a soluble Cr^{III}Cl$_3$(PN^{C18}P) precatalyst has allowed us, for the first time, to attempt detailed in situ characterization of the species generated during its activation by MAO under catalytic conditions. We can identify the sequential major species—**3**, **4**, and **7**—by their spectral signatures and show that (i) they account for most or all of the Cr in solution, and (ii) none of them is relevant to catalysis. At present, the Cr^{I} species **5** appears to be the most viable candidate for the ethylene trimerization catalyst or catalyst precursor, even though it does not appear to accumulate to more than a small percent of the total, implying it would have to be highly active, because it does react with ethylene. Alternatively, **5** could be yet another red herring, such that some species at low concentration that we have not been able to observe at all with our methodology is the active catalyst. Because **7** is the main species present (~94%) when activity is highest, even though all the indications so far argue against its participation in catalysis, its identification will be key to developing a more complete picture of the MAO reaction scheme. It must be noted, however, that MAO can also be involved in deactivation processes,[42] which could produce dormant states that reduce the number of chromium species available to react with substrates. Ongoing work is focused on further characterizing the reaction intermediates observed, with the aim of identifying catalyst compositions and conditions that most favor generation of the active species.

ASSOCIATED CONTENT

Supporting Information

Experimental details, ligand synthesis and characterization, spectroscopic data, and catalytic results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(32) Variable temperature ^{2}H NMR spectra (Supporting Information Figure S1) show that the methoxy groups in **2** exchange readily in solution, similar to those in **1** (see ref 7).

(33) Modified MAO (MMAO, see Supporting Information), which contains butyl in addition to methyl groups, was used in this study. All references to MAO hereafter refer to the use of MMAO.

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