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Ethylene Tetramerization with Cationic Chromium(I) Complexes

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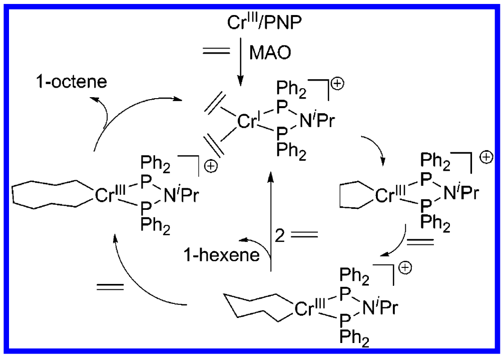
Various $[Cr(CO)_4(P\cap P)]^+$ complexes have been synthesized and tested for the tetramerization of ethylene to give principally 1-octene. The effect of the anion has been investigated, and it has been found that for successful catalysis an extremely weakly coordinating anion is required. This study shows that when $[Al(OC(CF_3)_3)_4]^-$ is employed as the anion, along with triethylaluminum and PNP^{iPr} as the coordinated diphosphine, the system is active for the tetramerization of ethylene. This is the first example of Cr^I being used as a catalyst precursor for selective tetramerization and gives evidence toward the catalytic cycle acting through a $Cr^I \rightarrow Cr^{III}$ cationic mechanism.

Introduction

In recent years there has been a considerable amount of work carried out on both the tri- and tetramerization of ethylene to produce 1-hexene and 1-octene, respectively.[1] For the most part, this has been due to increasing demand for these olefins as comonomers in the polymer industry. A variety of highly active Cr-based systems have been developed for both trimerization[2−4] and tetramerization,[5] as well as a number of trimerization catalysts based upon other early transition metals.[6,7] Sasol has developed a highly active tetramerization system with the PNP family of ligands and methylaluminoxane (MAO) as a cocatalyst. It has been shown by our research group, through the use of deuterium labeling, that the catalysis proceeds via a metallocycle mechanism.[8] It is generally believed that the cocatalyst MAO acts upon the Cr precursor to generate a cationic species as the catalytically active complex. Thus, in the highly active Cr/PNP^R ($PNP = Ph_2PN(R)PPh_2$) system it is expected that the generated species must be in oxidation state +1, as the PNP is believed to remain neutral after the system has been activated. This would lead to a cationic $Cr^I \rightarrow Cr^{III}$ mechanism as shown in Scheme 1. Bercaw and co-workers have also provided evidence for a metallocyclic $Cr^I \rightarrow Cr^{III}$ mechanism for related Cr−PNP trimerization catalysts.[9]

Scheme 1. Cationic Metallocycle Mechanism Proposed for the Cr/PNP Ethylene Tetramerization System



In the tetramerization process a high MAO to Cr ratio is required, which is undesirable due to the high cost of MAO. Considerable research has taken place to find alternative cocatalysts that display similar catalytic productivity and selectivity to MAO. We recently reported the use of $[Ph_3C][B(C_6F_5)_4]$ in combination with triethylaluminum, $AlEt_3$, as a replacement for MAO.[10] While successful in terms of generating active tetramerization systems, with liquid fraction selectivities similar to that obtained with MAO, this alternative activator system generated catalysts with very short lifetimes. This short catalyst lifetime is due to very fast exchange reactions between the borate anion and excess trialkylaluminum, which leads to rapid anion degradation, a more full discussion of this topic having been disclosed previously.[10]

In the search for alternative anions that might be more resistant to degradation of this kind, we studied the alternative activator system trityl tetrakis[perfluoro-*tert*-butoxy]aluminate

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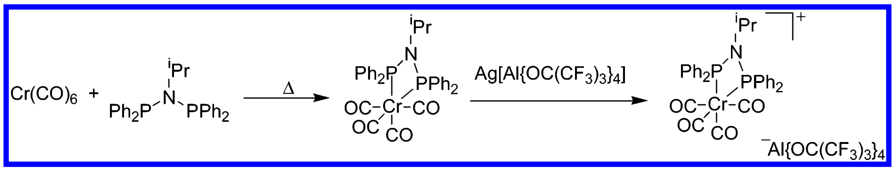
Scheme 2. Synthesis of $[Cr(CO)_4(PNP^{iPr})][1]$



$([Ph_3C][Al(OC(CF_3)_3)_4]$, $[Ph_3C][\mathbf{1}])$ in combination with $AlEt_3$. The results of these studies have been reported recently and include an NMR study illustrating the stability of anion [**1**] in the presence of excess trialkylaluminum.[11] It is believed that the presence of Et_3Al is required for alkylation of the Cr^{III} precursor, whereupon alkyl abstraction and reductive elimination can occur to generate a cationic Cr^I active species. While such catalyst generation from an inexpensive Cr^{III} precatalyst is most convenient from a process perspective, it affords little information regarding the oxidation state of the metal during catalysis. An alternative approach would be to start from a Cr^I species, as such a catalyst, if active, would provide valuable insight into the likely oxidation states of the active species. Herein, we report the synthesis and isolation of cationic Cr^I aluminates and their subsequent testing under tetramerization conditions. We show for the first time that Cr^I complexes can lead to effective catalysts for this transformation and provide further evidence for a $Cr^I \rightarrow Cr^{III}$ catalytic cycle.[12,13]

Results and Discussion

Synthesis of Cationic Cr^I Aluminate Complexes. The majority of low-valent Cr complexes in the literature have carbonyls present as a stabilizing ligand. Using a published method $Cr(CO)_4PNP^{iPr}$ was prepared in near quantitative yield.[14] Crystals of $Cr(CO)_4PNP^{iPr}$ suitable for X-ray analysis were grown by slow cooling of a hot DCM/MeOH solution.[12,15] To perform the one-electron oxidation of Cr^0 to Cr^I, it has been shown by Connelly and co-workers that the reaction of $AgBF_4$ with $Cr(CO)_4(dppm)$ (dppm = bis(diphenylphosphino)methane) at room temperature in DCM gives $[Cr(CO)_4(dppm)][BF_4]$.[16] The synthesis of the required $Ag(CH_2Cl_2)[\mathbf{1}]$ has been reported by Krossing[17] and was prepared as described from the lithium salt. Using a method analogous to that of Connelly, $[Cr(CO)_4(PNP^{iPr})][\mathbf{1}]$ was prepared (Scheme 2) in near quantitative yield as a deep blue solid with a magnetic moment of $\mu_{eff} = 1.83\ \mu_B$, which confirms that the complex is low-spin d^5, as expected for a Cr^I carbonyl. The IR spectrum shows three carbonyl stretches at 2086, 2032, and 1963 cm^{-1}, which is a shift toward higher wavenumbers compared to the corresponding neutral Cr^0 complex (2005, 1920, and 1888 cm^{-1}), as expected upon moving from a neutral to a charged species. The ^{19}F NMR (CD_2Cl_2) shows a singlet peak at −76.0 ppm with a half-height width $(\Delta_{1/2})$ of 11.5 Hz. It has been shown by Köhn et al. that the broadening of the ^{19}F NMR signal of a fluorinated anion indicates an interaction with the paramagnetic cation,[18] ion-pairing being deemed present when $\Delta_{1/2}$ is in the region 100−300 Hz or greater. Hence, it can clearly be seen that **1** is weakly coordinating in $[Cr(CO)_4(PNP^{iPr})][\mathbf{1}]$ (cf. $\Delta_{1/2}$ of Li[**1**], 3 Hz).

Crystals of $[Cr(CO)_4(PNP^{iPr})][\mathbf{1}]$ suitable for X-ray analysis were grown from toluene/petroleum ether, 40:60 (see Figure 1). Due to a high degree of rotational isomerism of the CF_3 groups, the refinement of the anion reveals some significant disorder. However, the refined structure obtained for the Cr cation is of good quality and shows a similar coordination geometry to the neutral Cr^0 complex. Notably four separate structure determinations were obtained from different crystals of this material, and all displayed similar disorder within the anion fragment. The shortest cation−anion distances are 2.792 Å intramolecularly and 2.839 Å intermolecularly, corresponding to interactions between a fluorine and a carbonyl oxygen (F13−O34 and F33−O32, respectively).[19] The disparity between the two Cr−P bonds lengths of 0.4 Å is of interest, notably that the Cr−P(2) bond, which is the longer of the two, resides *trans* to the carbonyl group, showing the intramolecular interaction with the anion.

In order to probe the effect of the N atom within the ligand backbone upon catalysis, the oxygen and carbon analogues were examined. The preparation of $[Cr(CO)_4(POP)][\mathbf{1}]$ (POP = $Ph_2P{-}O{-}PPh_2$) proceeded smoothly from the known precursor $[Cr(CO)_4(POP)]$. $Ph_2P{-}O{-}PPh_2$ is not isolable as a discrete compound, existing in the isomeric form $Ph_2P{-}P({=}O)Ph_2$; however, it has been shown by Wong et al.[20] that when heating the diphosphine monoxide with $Cr(CO)_6$, rearrangement takes place upon coordination to give the desired $[Cr(CO)_4(POP)]$.

In contrast, the action of $Ag(CH_2Cl_2)[\mathbf{1}]$ upon $[Cr(CO)_4(dppm)]$ (dppm = bis(diphenylphosphino)methane) did not yield the desired $[Cr(CO)_4(dppm)][\mathbf{1}]$, but gave a new species isolated as a pink-purple-colored solid. This material, which eluded positive identification, exhibited two broad signals in the ^{31}P NMR spectrum [δ 15.4 and 11.1] and a range of unassignable signals in the ^1H NMR spectrum. This unexpected reactivity could be the result of the acidic methylene protons of dppm,[21] or alternatively that nucleophilic attack upon phosphorus leading to cleavage of the P−C backbone bond is not without precedent.[22] Given the failure of the dppm complex to oxidize cleanly, the dippm (dippm = bis(diisopropylphosphino)methane) analogue was examined in the belief that the methylene protons

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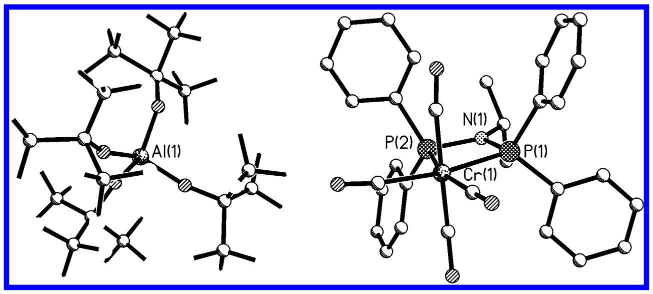

Figure 1. Molecular structure of [Cr(CO)$_4$(PNP$^{i\mathrm{Pr}}$)][**1**]. Selected bond distances (Å) and angles (deg): Cr(1)−P(1) 2.263(7); Cr(1)−P(2) 2.660(8); Cr(1)−C(31) 1.90(3); Cr(1)−C(32) 2.01(3); Cr(1)−C(33) 1.87(4); Cr(1)−C(34) 1.87(3); P(1)−Cr(1)−P(2) 62.2(2); P(1)−N(1)−P(2) 95.8(9).

may be less acidic and that the phosphorus center would be more electron rich and hence less prone to nucleophilic attack.[21] The synthesis of the precursor complex [Cr(CO)$_4$(dippm)] was facile; however, the subsequent oxidation to the desired [Cr(CO)$_4$(dippm)][**1**] did not proceed, despite repeated attempts, instead appearing to decompose. Hence, in order to access a ligand backbone with a carbon bridge, the two-carbon dppe analogue [Cr(CO)$_4$(dppe)][**1**] (dppe = bis(diphenylphosphino)ethane) was prepared from the known [Cr(CO)$_4$(dppe)], the oxidation proceeding smoothly on this occasion.

To determine the effect of the anion upon catalysis, other Cr$^{\mathrm{I}}$−PNP complexes with different weakly coordinating anions were prepared, namely, [Cr(CO)$_4$(PNP$^{i\mathrm{Pr}}$)][BF$_4$] and [Cr(CO)$_4$(PNP$^{i\mathrm{Pr}}$)][PF$_6$] from [Cr(CO)$_4$(PNP$^{i\mathrm{Pr}}$)] and the corresponding silver salt. The measured $\Delta_{1/2}$ of the ^{19}F peaks for the PF$_6$ and the BF$_4$ complex were found to be 140 and 625 Hz, respectively, and are clearly indicative of stronger interactions between the anion and cation than was found in [Cr(CO)$_4$(PNP$^{i\mathrm{Pr}}$)][**1**].

Carbonyl Ligand Removal. In order that the Cr$^{\mathrm{I}}$ cations may become active catalysts, it was envisaged that the carbonyl ligands must be removed from the coordination sphere of Cr, such that free coordination sites exist for ethylene to coordinate and in turn undergo oxidative coupling to form the theorized metallocyclopentane. Three methods were attempted to remove the carbonyl ligands; (i) by UV photolysis,[23] (ii) via reaction with Et$_3$Al, and (iii) via reaction with Me$_3$NO,[24] all of which are known procedures for carbonyl abstraction. Surprisingly, it was found that refluxing a mixture of Me$_3$NO and [Cr(CO)$_4$(PNP$^{i\mathrm{Pr}}$)][**1**] in acetonitrile under nitrogen gave no reaction, as indicated by the unchanging IR spectrum. In contrast, a DCM solution of [Cr(CO)$_4$(PNP$^{i\mathrm{Pr}}$)][**1**] following addition of 100 equiv of AlEt$_3$ (1.0 M in hexanes) showed a complete loss of signal, within 1 min, in the region of the IR spectrum associated with metal-bound carbonyl groups. A concomitant color change from royal blue to brown was observed, with all of the material remaining in solution for at least 15 min, indicating the loss of carbonyl signals, was not an artifact of carbonyl species precipitating from solution.

A DCM solution of [Cr(CO)$_4$(PNP$^{\mathrm{iPr}}$)][**1**] was placed in an IR solution cell containing a UV transparent window perpendicular to the IR windows for simultaneous photolysis and data acquisition of the sample. The solution was subjected to UV radiation with a power of 3 W cm^{-2} for 30 s periods and a quiescent period of 90 s between irradiations. A series of IR spectra were taken during the quiescent period. As time progressed, the three carbonyl bands of [Cr(CO)$_4$(PNP$^{i\mathrm{Pr}}$)][**1**] diminished with concomitant formation of three new carbonyl stretching frequencies at 2005, 1920, and 1888 cm^{-1}. Surprisingly, this suggests formation of the Cr^0 species, [Cr(CO)$_4$(PNP$^{i\mathrm{Pr}}$)], and from initial inspection of the IR data (see Figure 2), it also appears as though this conversion is quantitative. However, through determination of absorption coefficients from standard solutions of both Cr$^{\mathrm{I}}$ and Cr^0 species, it is found that only 33% of the initial Cr$^{\mathrm{I}}$ inventory can be accounted for by formation of [Cr(CO)$_4$(PNP$^{i\mathrm{Pr}}$)]. This suggests that the remaining Cr metal no longer possessed coordinated CO ligands.

Ethylene Tetramerization. When a Cr$^{\mathrm{III}}$ precursor is used for the tetramerization of ethylene, both an alkylating and alkyl abstracting agent is required. This can be either a single substance such as MAO or two different compounds each playing a role, for example Et$_3$Al (alkylating) and the trityl cation (alkyl abstracting). However, in the Cr$^{\mathrm{I}}$ precursor case neither of these criteria are required, provided a route to remove the carbonyl ligands is utilized instead. Tetramerization was attempted by either photolyzing the solution or reacting it with Et$_3$Al to remove the carbonyl ligands, the results being shown in Table 1As expected, in the absence of a carbonyl-abstracting agent, [Cr(CO)4(PNP$^{i\mathrm{Pr}}$)][**1**] is inactive for ethylene tetramerization (entry 1). To determine whether an active catalyst could be formed with only activation of the complex by UV photolysis, [Cr(CO)$_4$(PNP$^{i\mathrm{Pr}}$][**1**] (20 μmol) was dissolved in toluene (10 cm^3) and photolyzed under ethylene (8 bar). The ethylene was used to stabilize any low-coordinate species that are formed in the photolysis process. After 10 min the solution was transferred under positive pressure of ethylene to an autoclave containing methylcyclohexane (MCH) at 60 °C. The reactor was pressurized with ethylene (40 bar) and the reactor stirred vigorously for 1 h. Upon cooling and venting of the reactor, the liquid fraction was analyzed and no oligomers were found to be present (entry 2). Hence, this procedure was repeated in the presence of 400 equiv of AlEt$_3$ (entry 3). A 25 min induction period was observed to occur in the reactor (as indicated by gas uptake data), after which an active catalyst was successfully generated, and the autoclave was stirred for a further 50 min. It should be noted in this regard that the role of AlEt$_3$ may also be to act as an additional poison scavenger (aside from CO), and hence an amount may be required to protect the active species, as is often the case in ethylene polymerization chemistry. The failure of irradiation alone to activate the catalyst may also be due to a lack of scavenger to permanently remove the carbonyl ligands from Cr.

In contrast, when 50−400 equiv of AlEt$_3$ was employed without the use of photolysis, [Cr(CO)$_4$(PNP$^{i\mathrm{Pr}}$][**1**] was found to be immediately active for the trimerization and tetramerization of ethylene (entries 4−7). The C$_6$ and C$_8$ selectivities obtained closely match those obtained with a Cr$^{\mathrm{III}}$/MAO catalyst system under the same conditions, along with the formation of small amounts of methylcyclopentane and methylenecyclopentane.[8] From this, we conclude that similar active species are present in both cases. The productivity obtained is dependent upon the amount of AlEt$_3$ employed relative to Cr with an optimum activity around 200 equiv (entry 6). A very low activity was observed with only 50 equiv of AlEt$_3$, and so no further exploration to lower amounts was undertaken.

It is notable that the use of photolysis seems to reduce the productivity of the catalyst (cf. entries 3 and 7). This may be related to the above observation (*vide supra*) that irradiation leads to some degradation (∼33% of Cr) of the Cr cation back to Cr(CO)$_4$(PNP$^{i\mathrm{Pr}}$).

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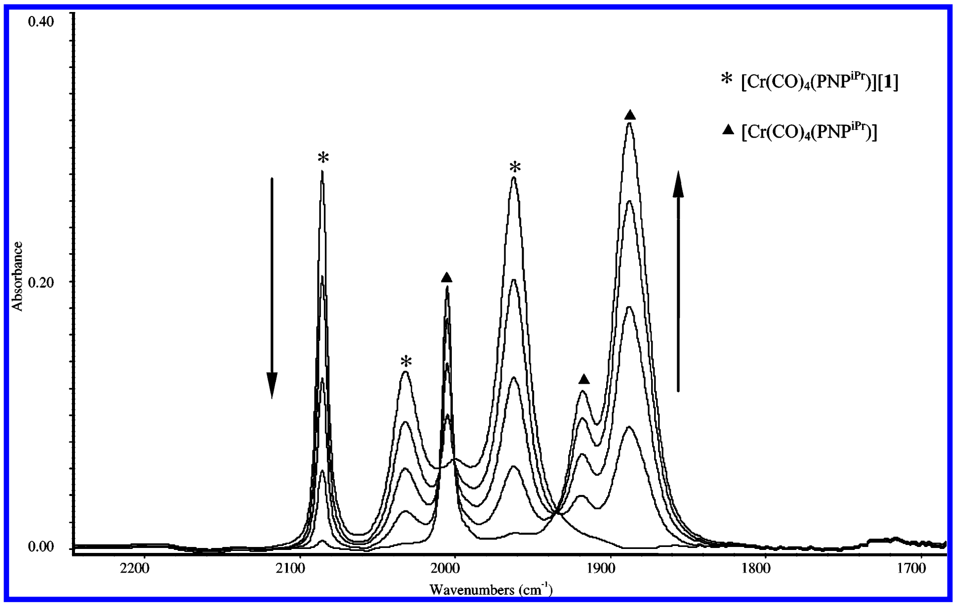

Figure 2. IR spectra of $[Cr(CO)_4(PNP)]$[**1**] undergoing UV photolysis, showing the evolution with time, as the initial species disappears and new signals corresponding to the neutral $[Cr(CO)_4(PNP)]$ grow in.

Table 1. Ethylene Tetramerization with $[Cr(CO)_4(P{-}P)][1]$ Complexes Activated with Photolysis of Trialkyl Aluminum

entry	catalyst	photolysis (min)	AlR_3 (equiv)	PE (wt %)	C_6 (wt %) $(1 - C_6)^b$	C_8 (wt %) $(1 - C_8)^b$	productivity (g/g Cr)	activity (g/g Cr/h)
1	$[Cr(CO)4(PNP^{iPr})]$[**1**]	0	0				0	0
2	$[Cr(CO)_4(PNP^{iPr})]$[**1**]	10	0				0	0
3	$[Cr(CO)_4(PNP^{iPr})]$[**1**]	10	$AlEt_3$ (400)	1.2	21.4 (76.9)	71.6 (98.7)	85 000	85 000
4	$[Cr(CO)_4(PNP^{iPr})]$[**1**]	0	$AlEt_3$ (50)	1.8	24.8 (83.8)	67.2 (97.1)	10 600	10 600
5	$[Cr(CO)_4(PNP^{iPr})]$[**1**]	0	$AlEt_3$ (100)	0.2	20.4 (77.1)	72.8 (98.8)	83 900	83 900
6	$[Cr(CO)_4(PNP^{iPr})]$[**1**]	0	$AlEt_3$ (200)	1.1	21.4 (78.8)	70.7 (99.0)	139 800	139 800
7	$[Cr(CO)_4(PNP^{iPr})]$[**1**]	0	$AlEt_3$ (400)	0.23	21.4 (78.1)	72.4 (99.0)	126 300	126 300
8	$[Cr(CO)_4(PNP^{iPr})]$[**1**]	0	$^iBu_3Al$ (400)	2.4	21.2 (79.0)	70.2 (100)	28 400	28 400
9	$[Cr(CO)_4(PNP^{iPr})]$[**1**]	0	$^iBu_3Al$ (100) $AlEt_3$ (300)	0.8	21.7 (76.5)	72.7 (99.0)	67 200	67 200
10	$[Cr(CO)_4(PNP^{iPr})][PF_6]$	0	$AlEt_3$ (400)				0	0
11	$[Cr(CO)_4(PNP^{iPr})][BF_4]$	0	$AlEt_3$ (400)				0	0
12	$Cr(CO)_4(PNP^{iPr})$	0	$AlEt_3$ (100)	59.4	15.5 (65.1)	20.6 (35.4)	800^d	1600
13	$[Cr(CO)_4(POP)]$[**1**]	0	$AlEt_3$ (400)	0			0	0
14	$[Cr(CO)_4(POP)]$[**1**]^c	0	$AlEt_3$ (400)	0			0	0
15	$[Cr(CO)_4(dppe)]$[**1**]	0	$AlEt_3$ (400)	10.4	24.2 (51.8)	46.7 (100)	6000	6000
16	$[Cr(CO)_4(dppe)]$[**1**]^c	0	$AlEt_3$ (100)	6.3	24.3 (58.9)	59.9 (97.6)	19 300	19 300

[a] Conditions: Cr (5 μmol), 10 mL of toluene, 90 mL of methylcyclohexane, 60 °C, ethylene pressure (40 bar). All runs (except entry 12) 60 min. [b] Selectivity to α-olefin within carbon length fraction. [c] Cr (20 μmol). [d] 30 min run.

A series of patents from Tosoh Corporation describe the use of triisobutyl aluminum to activate low-valent Cr precursors toward trimerization in conjunction with UV irradiation to remove carbonyl ligands.[25] Utilization of this alternative aluminum activator in our system (without UV photolysis) did indeed generate an active catalyst (entries 8 and 9); however, it was inferior to $AlEt_3$, so no further examination in the presence of UV photolysis was made.

In order to probe the effect of the anion upon catalysis, the complexes with the PF_6 and BF_4 anions in place of the aluminate, [**1**], were screened (entries 10 and 11), no activity being observed in either case. This is rationalized as an effect of the relatively strongly coordinating nature of these anions (cf. [**1**]) to the cation (*vide supra*), which is believed to have a negative effect upon the catalysis.

As a Cr^I precursor is theorized as the initiating species for tetramerization, it was of interest to screen the neutral parent carbonyl complex $Cr^0(CO)_4(PNP^{iPr})$ for catalytic activity (entry 12). This precatalyst source did display some limited activity toward tetramerization; however, the catalyst was both poorly active and primarily a polymerization system.

In order to better understand the implications of the N atom in the ligand backbone toward catalysis, the analogous compounds $[Cr(CO)_4(POP)]$[**1**] and $[Cr(CO)_4(dppe)]$[**1**] were tested (entries 13−16). However the POP analogue did not generate oligomers of any kind, indicating that this ligand does not support an active tetramerization catalyst. Meanwhile, the dppe analogue was moderately active and selective toward tetramerization, notably with similar liquid fraction selectivity to the reported Cr^{III}/dppe/MAO system,[5] suggesting that a similar Cr-active species is present in both cases. This suggests that the nature of the bridging atom is crucial to the catalysis and that

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simple modification of the bridge can lead to dramatic changes in catalytic performance.

Summary and Conclusions

A variety of Cr^0 and Cr^I carbonyl complexes of PNP and related ligands have been prepared and fully characterized. The evaluation of these complexes for the ethylene tetramerization reaction reveals that a Cr^I cation along with a weakly coordinating anion is required to produce an active system and that a trialkylaluminum reagent is necessary to abstract the carbonyl ligands from Cr and possibly to act as a poison scavenger. Aside from the postulated oxidative coupling believed to occur in the catalytic cycle, it is unlikely that under the conditions employed oxidation of the Cr to a higher oxidation state active species would take place. This conclusion, together with the near lack of activity displayed by a Cr^0 complex, lends further support for a cycle involving formally Cr^I and Cr^{III} active species. We have also demonstrated that MAO is not an indispensable cocatalyst in the tetramerization of ethylene, and this work opens the way for the further development of catalyst systems based on less expensive cocatalysts. Further work in this regard is ongoing and will be reported in due course.

Experimental Section

General Comments. All manipulations were carried out using standard Schlenk techniques or in a nitrogen glovebox, using solvents purified and dried via standard procedures. $Ag[Al\{OC(CF_3)_3\}_4]$,[17] $Ph_2PP({=}O)Ph_2$,[26] $Cr(CO)_4(POP)$,[20] $Cr(CO)_4(dppm)$,[27] $Cr(CO)_4(dippm)$,[27] $Cr(CO)_4(dppe)$,[27] and $Cr(CO)_4(PNP^{iPr})$[28] were prepared using literature procedures or slight modifications thereof.

Representative Procedure for Neutral Chromium Tetracarbonyl Species: $Cr(CO)_4(PNP^{iPr})$. A Schlenk flask was charged with $Cr(CO)_6$ (4.00 g, 18.2 mmol) and PNP^{iPr} (7.77 g, 18.2 mmol), and anhydrous diglyme (50 cm^3) was added. The mixture was heated to 160 °C for 2 h, after which time the resultant solution was allowed to cool. The solution was concentrated *in vacuo*, and MeOH (30 cm^3) was added. The solution was placed in the freezer and the resultant yellow powder collected by filtration, washed with MeOH (2 × 20 cm^3), and dried *in vacuo* (8.94 g, 83%). A portion was recrystallized from hot DCM/MeOH, which gave yellow blocks suitable for X-ray analysis. Anal. Calcd for $C_{31}H_{27}CrNO_4P_2$ (found): C, 62.95 (62.93); H, 4.60 (4.56); N, 2.37 (2.31).

$[Cr(CO)_4(PNP^{iPr})][1]$. A Schlenk flask was charged with $Cr(CO)_4(PNP^{iPr})$ (0.075 g, 0.13 mmol), and dichloromethane (15 cm^3) was added. Ag[**1**] (0.140 g, 0.13 mmol) was added to the solution, and an immediate color change to dark blue was observed. The mixture was allowed to stir for 1 h, after which a second portion of Ag[**1**] (0.13 mmol) was added. After stirring overnight the solution was filtered and the solvent was removed *in vacuo*. The resultant blue solid was washed with petrol 40:60 (2 × 20 cm^3) and dried *in vacuo* (0.150 g, 74%). Anal. Calcd for $C_{47}H_{27}AlCrF_{36}NO_8P_2$ (found): C, 36.22 (36.19); H, 1.75 (1.73); N, 0.90 (0.87). $\mu_{eff} = 1.83\ \mu_B$. ^{19}F NMR (CD_2Cl_2, 295 K): δ −76.0 (s, $\nu_{1/2} =$ 11.5 Hz). IR (CH_2Cl_2): $\nu_{CO} = 2086\ cm^{-1}$, $\nu_{CO} = 2032\ cm^{-1}$, $\nu_{CO} = 1963\ cm^{-1}$.

$[Cr(CO)_4(PNP^{iPr})][BF_4]$. A Schlenk flask was charged with $Cr(CO)_4(PNP^{iPr})$ (0.61 g, 1.03 mmol), and dichloromethane (15 cm^3) was added. $AgBF_4$ (0.20 g, 1.03 mmol) was added to the solution, with a concomitant color change to dark blue. The mixture was allowed to stir for 1 h, after which it was filtered and the solvent was removed *in vacuo*. The resultant blue solid was washed with petrol 40:60 (2 × 20 cm^3) and dried *in vacuo* (0.54 g, 77%). Anal. Calcd for $C_{31}H_{27}BCrF_4NO_4P_2$ (found): C, 54.89 (54.98); H, 4.01 (4.08); N, 2.06 (2.07). $\mu_{eff} = 1.63\ \mu_B$. ^{19}F NMR (CD_2Cl_2, 295 K): δ −149.7 (br s, $\nu_{1/2} = 625$ Hz). IR (CH_2Cl_2): $\nu_{CO} = 2085\ cm^{-1}$, $\nu_{CO} = 2032\ cm^{-1}$, $\nu_{CO} = 1960\ cm^{-1}$.

$[Cr(CO)_4(PNP^{iPr})][PF_6]$. A Schlenk flask was charged with $Cr(CO)_4(PNP^{iPr})$ (0.59 g, 1.00 mmol), and dichloromethane (15 cm^3) was added. $AgPF_6$ (0.25 g, 1.00 mmol) was added to the solution, with a concomitant color change to dark blue. The mixture was allowed to stir for 1 h, after which it was filtered and the solvent was removed *in vacuo*. The resultant blue solid was washed with petrol 40:60 (2 × 20 cm^3) and dried *in vacuo* (0.62 g, 84%). Anal. Calcd for $C_{31}H_{27}CrF_6NO_4P_3$ (found): C, 50.56 (50.65); H, 3.70 (3.71); N, 1.90 (1.89). $\mu_{eff} = 1.78\ \mu_B$. ^{19}F NMR (CD_2Cl_2, 295 K): δ −69.6 (d, $^1J_{P-F} = 709$ Hz, $\nu_{1/2} = 140$ Hz). IR (CH_2Cl_2): $\nu_{CO} = 2085\ cm^{-1}$, $\nu_{CO} = 2032\ cm^{-1}$, $\nu_{CO} = 1962\ cm^{-1}$.

$[Cr(CO)_4(POP)][1]$. A Schlenk flask was charged with $Cr(CO)_4(POP)$ (0.095 g, 0.17 mmol), and dichloromethane (10 cm^3) was added. Ag[**1**] (0.200 g, 0.17 mmol) was added to the solution, an immediate darkening in color being observed. The mixture was allowed to stir overnight at RT, and a second portion of Ag[**1**] (0.17 mmol) was added, followed by stirring for a further 18 h. The solution was filtered, the solid was washed with petrol 40:60 (1 × 20 cm^3), and the combined fractions were reduced *in vacuo* to leave a green powder (0.191 g, 74%). Anal. Calcd for $C_{44}H_{20}AlCrF_{36}O_9P_2$ (found): C, 34.83 (34.60); H, 1.33 (1.43). ^{19}F NMR (CD_2Cl_2, 295 K): δ −76.1 (br s, $\nu_{1/2} = 12.7$ Hz).

$[Cr(CO)_4(dppe)][1]$. A Schlenk flask was charged with $Cr(CO)_4(dppe)$ (0.075 g, 0.13 mmol), and dichloromethane (10 cm^3) was added. Ag[**1**] (0.143 g, 0.13 mmol) was added to the solution, an immediate darkening in color being observed. The mixture was allowed to stir overnight at RT, and a second portion of Ag[**1**] (0.13 mmol) was added, followed by stirring for a further 18 h. The solution was filtered, the solid was washed with petrol 40:60 (1 × 20 cm^3), and the combined fractions were reduced *in vacuo* to leave a purple powder (0.186 g, 94%). Anal. Calcd for $C_{46}H_{24}AlCrF_{36}O_8P_2$ (found): C, 36.12 (36.01); H, 1.58 (1.54). ^{19}F NMR (CD_2Cl_2, 295 K): δ −76.1 (br s, $\nu_{1/2} = 5.6$ Hz). IR (CH_2Cl_2): $\nu_{CO} = 2084\ cm^{-1}$, $\nu_{CO} = 2031\ cm^{-1}$, $\nu_{CO} = 1970\ cm^{-1}$.

Tetramerization. Ethylene tetramerization was carried out in a 300 cm^3 stainless steel reactor with mechanical stirring. The oven-dried vessel was purged with N_2 followed by ethylene, charged with methylcyclohexane (90 cm^3), and heated to 60 °C. The catalyst solution was prepared by dissolving the required amount of catalyst in toluene (10 cm^3) and adding the required amount of trialkylaluminum (AlR_3). The solution was injected into the prepared autoclave, and the reactor was immediately charged with 40 bar of ethylene and maintained at this pressure for the duration of the reaction. After 1 h the reactor was cooled in an ice bath, the excess ethylene was bled, and an internal standard was added (nonane, 1000 μL). After quenching with MeOH followed by 10% HCl, the organic phase was analyzed by GC, and the while solids were filtered, washed, dried, and weighed.

After the catalyst was photolyzed prior to the reaction, the catalyst solution (with or without AlR_3) was transferred to a glass Buchi reactor, which was subsequently pressurized with ethylene (8 bar). The solution was then photolyzed with UV light from a Hg-discharge lamp with the output being directed with a light guide. The power of the lamp at the end of the light guide was 3 W cm^{-2}. The solution was photolyzed with stirring for 10 min, after which the ethylene was slowly vented and the solution transferred to the prepared autoclave by cannula.

IR Spectroscopy. Infrared spectra were recorded on a Nicolet Nexus instrument fitted with a MCT-High D* detector. Absorption

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coefficients were determined from IR spectra of standard solutions in dichloromethane using a solution cell with a path length of 1 mm. The absorbance as a function of concentration was determined at 1888 cm^{-1} for $[Cr(CO)_4(PNP^{iPr})]$ and 2085 cm^{-1} for $[Cr(CO)_4(PNP^{iPr})][\mathbf{1}]$ with a linear baseline defined by the limits 2080 and 1788 cm^{-1} in each case. The photolysis experiment was carried out in a variable path length solution cell with a third UV-transparent window perpendicular to the IR beam for irradiation of the solution. The solution was photolyzed using an EXFO Acticure 4000 spot curing system fitted with a liquid light guide. The solution was irradiated with a power of 3 W cm^{-2}.

X-ray Crystallography. Data were collected using a Rigaku MM007 Mo high-brilliance rotating anode/confocal optics with a Rigaku Mercury detector, for $[Cr(CO)_4(PNP^{iPr})]$, whereas $[Cr(CO)_4(PNP^{iPr})][\mathbf{1}]$ used a Rigaku Saturn92 detector on a Rigaku MM007 Cu high-brilliance rotating anode/confocal optics, and the data were corrected for absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 values of all data (G. M. Sheldrick, SHELXTL, Bruker AXS Madison WI, 2001, version 6.1).

$Cr(CO)_4(PNP^{iPr})$. $C_{31}H_{27}CrNO_4P_2$, $M = 591.48$, yellow, crystal size 0.3 × 0.2 × 0.1 mm, triclinic, $P\bar{1}$, $a = 10.799(2)$ Å, $b = 15.442(3)$ Å, $c = 17.983(4)$ Å, $\alpha = 90.504(9)°$, $\beta = 106.818(7)°$, $\gamma = 95.228(7)°$, $V = 2856.8(9)$ Å^3, $Z = 4$ (two crystallographically independent molecules), $D_{calcd} = 1.375$ Mg m^{-3}; Mo Kα radiation ($\lambda = 0.71073$ Å), $\mu = 0.735$ mm^{-1}, $T = 93(2)$ K; 15 687 data (9302 unique, $R_{int} = 0.0400$), conventional $R = 0.0665$ for 6658 reflections with $F_o^2 > 2\sigma F_o^2$, $S = 1.127$ for 704 parameters. Residual electron density extremes were 0.478 and −0.496 e Å^{-3}.

$[Cr(CO)_4(PNP^{iPr})][\mathbf{1}]$. Very poor crystal quality precluded a good analysis; several different crystals were examined, using both Mo and Cu radiation. The best Cu data set was selected and is reported here. $C_{31}H_{27}CrNO_4P_2$, $C_{16}F_{36}AlO_4$, $M = 1558.62$, blue platelet, crystal size 0.1 × 0.1 × 0.01 mm, monoclinic, $P2_{(1)}/c$, $a = 14.7195(13)$ Å, $b = 25.217(2)$ Å, $c = 16.4329(14)$ Å, $\beta = 103.915(3)°$, $V = 5920.6(9)$ Å^3, $Z = 4$, $D_{calcd} = 1.749$ Mg m^{-3}; Cu Kα radiation ($\lambda = 1.54178$ Å), $\mu = 3.787$ mm^{-1}, $T = 173(2)$ K; 28 807 data (4661 unique, $R_{int} = 0.1554$), conventional $R = 0.2615$ for 3816 reflections with $F_o^2 > 2\sigma F_o^2$, $S = 3.020$ for 286 parameters. All carbon and fluorine atoms were refined isotropically, with the CF_3 groups having fixed carbon thermal parameters and the fluorines riding thermal parameters in idealized geometries. Residual electron density extremes were 2.268 and −1.956 e Å^{-3}.

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Supporting Information Available: Crystallographic data, in CIF format, for structures reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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