Organometallics **2006,** *25,* 2743−2749

Ethylene Trimerization Catalysts Based on Chromium Complexes with a Nitrogen-Bridged Diphosphine Ligand Having *ortho*-Methoxyaryl or *ortho*-Thiomethoxy Substituents: Well-Defined Catalyst Precursors and Investigations of the Mechanism

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Received July 19, 2005

Chromium-based ethylene trimerization catalyst precursors (($\mathrm{PNP^{OMe}}$-d_{12})$\mathrm{CrPh_3}$ (**4**) and ($\mathrm{PNP^{OMe}}$-d_{12})$\mathrm{CrPh_2Cl}$ (**7**)) having a bis(diphenylphosphino)amine ligand (o-$\mathrm{CD_3OC_6H_4}$)$_2$PN($\mathrm{CH_3}$)P(o-$\mathrm{CD_3OC_6H_4}$)$_2$ (($\mathrm{PNP^{OMe}}$-d_{12}) = **1**) have been prepared and characterized. A thioether analogue (o-$\mathrm{CD_3SC_6H_4}$)$_2$PN($\mathrm{CH_3}$)P(o-$\mathrm{CD_3SC_6H_4}$)$_2$ (($\mathrm{PNP^{SMe}}$-d_{12}) = **2**) and its triphenylchromium complex ($\mathrm{PNP^{SMe}}$)$\mathrm{CrPh_3}$ (**5**) have also been synthesized. The solid-state structures of **4** and **7** display octahedral geometries with a κ^3-(P,P,O) coordination of $\mathrm{PNP^{OMe}}$ ligands having chromium−oxygen bond lengths of 2.29−2.44 Å. Compound **5** differs, exhibiting (S,P,S)-κ^3 coordination of the $\mathrm{PNP^{SMe}}$ ligand. The deuteromethyl groups allow for ^{2}H NMR characterization of these paramagnetic complexes in solution. Dynamic exchange processes occur in solution at room temperature to render all four of the methoxy or thioether groups equivalent on the ^{2}H NMR time scale; two distinct coalescence processes are observed by variable-temperature ^{2}H NMR spectroscopy for all compounds. The neutral species **4** and **7** react with ethylene (1 atm) by insertion into chromium−phenyl bonds with the release of styrene and ethylbenzene, but 1-hexene is not observed under these conditions. Activation of **4** by protonation and activation of **7** by halide abstraction in the presence of ethylene provide active trimerization catalysts that give turnover numbers for 1-hexene as high as 3000 mol 1-hexene•mol^{-1} Cr. These catalysts display comparable activity and selectivity for 1-hexene compared to the original BP system, where the catalyst is generated in situ from $\mathrm{CrCl_3(THF)_3}$, **1**, and MAO. Both the well-defined systems and the $\mathrm{CrCl_3(THF)_3/PNP^{OMe}}$/MAO system provide catalysts that undergo an initiation period followed by an apparent first-order decomposition process. Activated complexes **4** and **7** initiate trimerization primarily through ethylene insertion into the chromium−phenyl bond, followed by β-hydrogen elimination and reductive elimination to give the active species, rather than via reductive elimination of biphenyl.

Introduction

Transition metal-catalyzed ethylene oligomerization typically produces a broad range of α-olefins.[1] Linear α-olefins, especially 1-hexene and 1-octene, are desirable comonomers for the production of linear low-density polyethylene.[2] In 1989 Briggs reported the chromium-catalyzed selective trimerization of ethylene to produce 1-hexene.[3] Several recent reports describe other chromium-based catalysts that can carry out this process with high selectivity.[4] Catalysts based on titanium,[5] tantalum,[6] and vanadium[7] complexes have also been found to promote ethylene trimerization.

BP has described a particularly active and selective chromium-based ethylene trimerization catalyst that is comprised of a Cr(III) precursor,[8] a bis(diphosphino)amine ligand ((o-MeO-$\mathrm{C_6H_4}$)$_2$PN($\mathrm{CH_3}$)P(o-MeO−$\mathrm{C_6H_4}$)$_2$, ($\mathrm{PNP^{OMe}}$-d_{12}) = **1**), and activation by methylaluminoxane (MAO) (eq 1).[9]

$$\underset{(1-20\ \text{bar})}{\text{ethylene}} \xrightarrow[\text{300 equiv MAO, toluene}]{\mathrm{CrCl_3(THF)_3} + \mathbf{1}} \text{1-hexene} \tag{1}$$

In the preceding article we describe the synthesis and characterization of chromium(0) carbonyl, chromium(III) halide,

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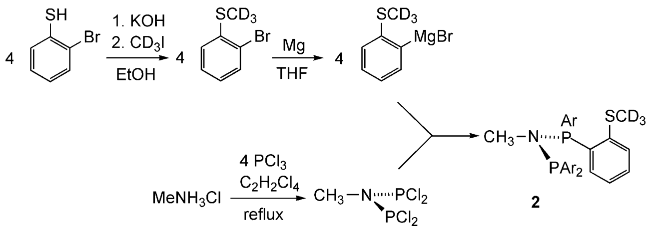
[8] Cr(II) has also been shown to be active. See ref 9.

10.1021/om0506062 CCC: $33.50

Scheme 1



halo-alkyl, and dibenzochromacylopentane complexes having $\mathrm{PNP^{OMe}}$-type ligands, along with some postulates for the general mechanism.[10] This catalytic cycle involves (i) initial coordination of 2 equiv of ethylene to a ligated Cr^{n} species, followed by (ii) oxidative coupling to form a chromacyclopentane of oxidation state Cr^{n+2}, (iii) ring expansion to seven by ethylene insertion, and (iv) rapid β-hydrogen elimination and reductive elimination of 1-hexene to regenerate Cr^{n}. More recently it has been suggested, and supported by DFT studies, that the release of 1-hexene from the chromacyloheptane intermediate is a concerted 3,7-hydrogen shift with formal two-electron reduction of the metal.[11,12]

In an effort to learn more about the PNP-chromium-based catalytic system, the synthesis, characterization, and reactivity of well-defined $[(\mathrm{PNP^{OMe}}\text{-}d_{12})\mathrm{Cr^{III}}]$ phenyl complexes have been investigated, along with the corresponding $(\mathrm{PNP^{SMe}}\text{-}d_{12})\mathrm{CrPh_3}$ ($\mathrm{PNP^{SMe}} = (o\text{-}\mathrm{CD_3S\text{-}C_6H_4})_2\mathrm{PN(CH_3)P}(o\text{-}\mathrm{CD_3S\text{-}C_6H_4})_2$). Part of this work was communicated previously.[13] Complexes of the general form $(\mathrm{PNP^{OMe}}\text{-}d_{12})\mathrm{CrPh_3}$ and $(\mathrm{PNP^{OMe}}\text{-}d_{12})\mathrm{CrPh_2X}$ (X = halide) have been prepared and characterized in solution and in the solid state. These two complexes can be activated stoichiometrically to catalyze ethylene trimerization, and the selectivities and activities of these catalysts have been compared to the $\mathrm{CrCl_3(THF)_3/PNP^{OMe}}$/MAO system. These well-defined catalyst precursors have allowed for study of the trimerization mechanism, as well as an examination of their initiation pathways.

Results and Discussion

Synthesis of Deuterated PNP Ligands. Because our target chromium complexes are paramagnetic Cr(III) species, PNP ligands were designed to have deuterated methyl groups on the methoxy or thiomethoxy position for the purpose of examining the complexes by ^{2}H NMR spectroscopy.[14] Synthesis of **1** may be accomplished by either a stepwise or a convergent route.[10] The thioether analogue **2**, $(o\text{-}\mathrm{CD_3S\text{-}C_6H_4})_2\mathrm{PN(CH_3)P}(o\text{-}\mathrm{CD_3S\text{-}C_6H_4})_2$ ($\mathrm{PNP^{SMe}}\text{-}d_{12}$), has been synthesized via the convergent route (Scheme 1).[15] The room-temperature ^{31}P NMR spectra of **1** and **2** show characteristic resonances at $\delta = 54$ ppm and $\delta = 50$ ppm in THF and characteristic ^{2}H resonances at $\delta = 3.60$ ppm and $\delta = 2.26$ ppm in dichloromethane, respectively.

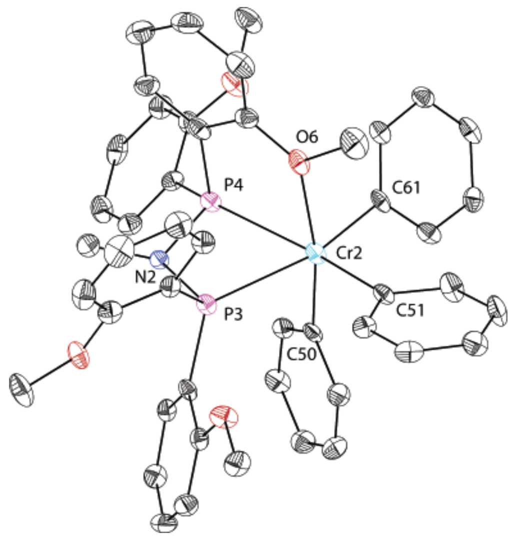


Figure 1. Molecular structure of **4** with 50% probability ellipsoids. Hydrogen atoms have been omitted. Selected bond distances (Å) and angles (deg) are as follows: $\mathrm{Cr_2{-}P_3}$ 2.6164(12); $\mathrm{Cr_2{-}P_4}$ 2.5044(12); $\mathrm{Cr_2{-}O_6}$ 2.279(3); $\mathrm{Cr_2{-}C_{50}}$ 2.060(4); $\mathrm{Cr_2{-}C_{51}}$ 2.092(4); $\mathrm{Cr_2{-}C_{61}}$ 2.081(4); $\mathrm{P_3{-}N_2{-}P_4}$ 105.92(17).

Synthesis of Chromium Triphenyl Complexes. $\mathrm{CrPh_3(THF)_3}$ (**3**) is one of few known tris(hydrocarbyl) chromium(III) complexes and thus provides an almost unique direct entry to tris(hydrocarbyl)Cr(III) complexes with these bis(diphenylphosphino)amine ligands. Its synthesis from $\mathrm{CrCl_3}$ and PhMgBr in THF was originally reported in 1959,[16] and its crystal structure was reported in 1983.[17] Reactions of the deuterated diphosphine ligands **1** and **2** with **3** in dichloromethane (reversibly) afford the desired $\mathrm{(PNP)CrPh_3}$ complexes in high yields. Both (PNP)-ligated chromium triphenyl complexes are significantly more stable than **3** toward reductive elimination of biphenyl in solution. Ligand **1** reacts with **3** to form $(\mathrm{PNP^{OMe}}\text{-}d_{12})\mathrm{CrPh_3}$ (**4**) as a red, microcrystalline solid in 68% yield (eq 2). Slow diffusion of petroleum ether into a dichloromethane solution of **4** at −35 °C provides crystals suitable for structural determination by X-ray diffraction. The solid-state structure of **4** shows the presence of two crystallographically independent molecules of **4** in the asymmetric unit with very similar structures; one of them is shown in Figure 1. The chromium center for **4** is hexacoordinate with the $\mathrm{PNP^{OMe}}$ ligand coordinated in a κ^3-(P,P,O) mode. The chromium−oxygen bond lengths of 2.279(3) and 2.293(2) Å are similar to the chromium−oxygen bond lengths in **3**. The structure also indicates that coordination of methoxy to chromium shortens the chromium−phosphorus bond distance of the chelating phosphorus by 0.11 Å to 0.17 Å, from 2.6164(12) Å to 2.5044(12) Å, and from 2.6597(12) Å to 2.4897(11) Å. The nitrogen is slightly pyramidal, with a sum of all three angles around it of 351.5°.

Although the solid-state structure of **4** indicates the coordination of one of the four methoxy groups, the room-temperature ^{2}H NMR spectrum in dichloromethane displays only a single peak at $\delta = 8.47$ ppm, suggesting that a dynamic process occurs in solution to render all four of the methoxy groups equivalent on the NMR time scale. Variable-temperature ^{2}H NMR spectra of **4** show two distinct coalescence points, as shown in Figure

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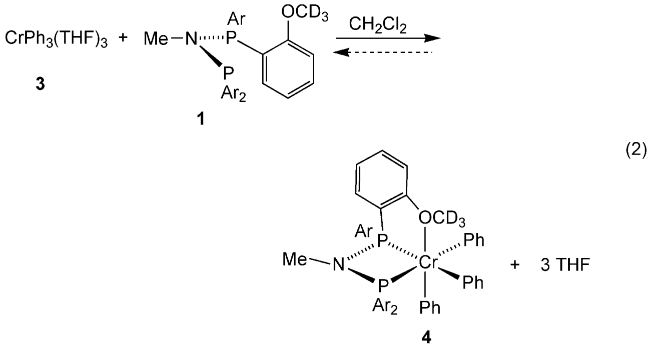
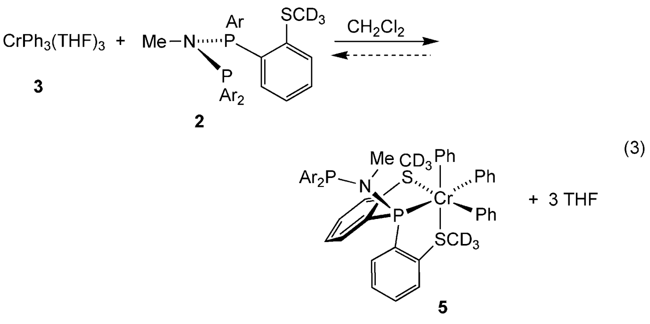


(2)

2. At −95 °C a very broad peak centered at $\delta = 50$ ppm is observed, as well as a single peak in the diamagnetic region ($\delta \approx 4$ ppm). As the sample is warmed, coalescence is observed at −75 °C, and at −50 °C two broad peaks are observed in a 1:1 ratio. As the solution is warmed further, the spectrum displays another coalescence at −41 °C; above this temperature, only one peak is observed for all four of the exchanging methoxy groups.

The spectrum at −95 °C is consistent with the static solid-state structure of **4**: the broad peak at $\delta = 50$ ppm is assigned to the Cr-coordinated methoxy group. The sharp peak in the diamagnetic region at $\delta \approx 4$ ppm is assigned to the three (inequivalent, but unresolved) uncoordinated methoxy groups. The occurrence of two separate exchange processes would account for the observed temperature dependence of the ^{2}H spectra. The faster exchange process that is evident from the spectrum at −75 °C involves the dissociation of the methoxy connected to one phosphorus (OMe^a), followed by recoordination of a methoxy group from the other phosphorus on the same hemisphere of the complex (OMe^b), as is discussed in the preceding article.[10]

Ligand **2** reacts with **3** to form (PNP^{SMe})CrPh$_3$ (**5**) as a brown powder in 56% yield (eq 3). Slow diffusion of petroleum ether into a dichloromethane solution of **5** at −35 °C provides crystals suitable for analysis by X-ray diffraction. The solid-state structure of **5** shows that the ligand binds to chromium through two sulfur atoms and a phosphorus (see Supporting Information). As compared with **4** this complex shows a quite different (S,P,S)-κ^3 binding mode for the PNP ligand with a dangling [-P(o-CD$_3$S-C$_6$H$_4$)$_2$]. Unfortunately, these crystals were suitable only for determination of connectivity in this structure, and reliable bond lengths have not been obtained for this complex.



(3)

The room-temperature ^{2}H NMR spectrum for **5** in dichloromethane displays a single peak at $\delta = -3.8$ ppm, indicating that like **4** it undergoes a dynamic exchange process in solution. An examination of the ^{2}H NMR spectra at −100 °C shows a very broad peak centered at $\delta = -38$ ppm, as well as a peak upfield at $\delta = 2.52$ ppm. Variable-temperature ^{2}H NMR spectra show two distinct coalescence points, one at −85 °C and another at 5 °C. Although comparisons of the relative intensities of very broad and less broad signals does not allow for a definitive conclusion, in the −100 °C spectrum the apparent relative integrations of the very broad downfield peak, as compared to the peak in the diamagnetic region, suggest that the static structure of **5** in solution involves coordination of a single thioether group to chromium, possibly in a fashion analogous to the structure of **4**. Although the solid-state structure of **5** involves one phosphine coordinated to chromium and the other dangling phosphine much farther away from the paramagnetic chromium center, a ^{31}P NMR signal for this complex is not

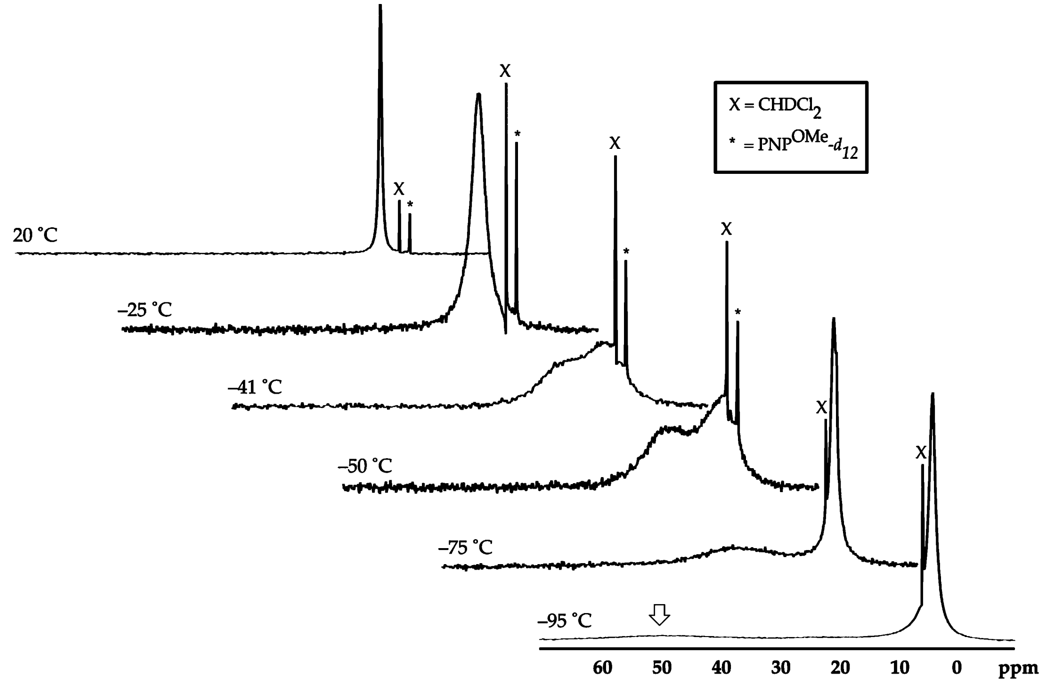


Figure 2. Variable-temperature ^{2}H NMR spectra of **4** in dichloromethane-d_2. The arrow indicates the broad peak assigned to the methoxy group coordinated to chromium in the static structure.

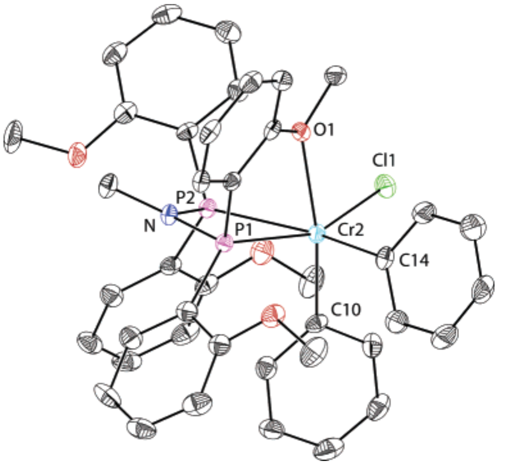
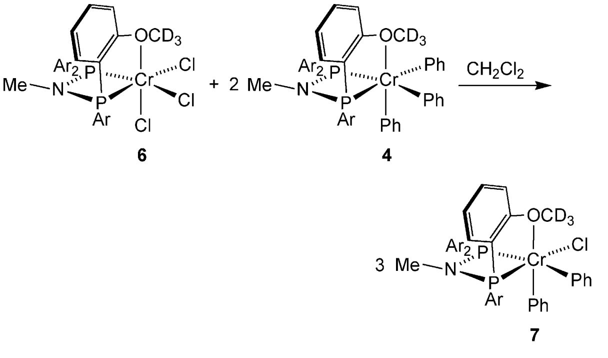


Figure 3. Molecular structure of **7** with 50% probability ellipsoids. Selected bond distances (Å) and angles (deg) are as follows: Cr−P_1 2.4414(6); Cr−P_2 2.6096(6); Cr−O_1 2.4371(14); Cr−Cl 2.3078(6); Cr−C_{10} 2.039(2); Cr−C_{14} 2.077(2); P1−N−P2 106.35(9).

observed, even at −95 °C, again suggesting that a structure analogous to that for **4** is accessible for **5** in solution.

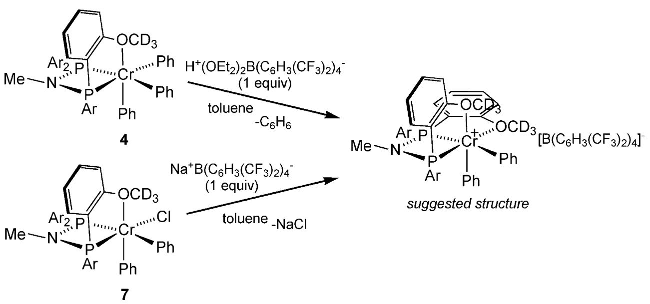
The spin states for chromium complexes **4** and **5** have been determined. Their EPR spectra at 20 K as toluene glasses are consistent with Cr(III) species with three unpaired electrons and $S = 3/2$ (see the Supporting Information).[18] Evans method determination of the solution magnetic susceptibility[19] for **4** indicates an effective magnetic moment (μ_{eff}) of 3.8 μ_B in dichloromethane, consistent with a quartet ground state with three unpaired electrons.

Synthesis of Chromium Phenyl Halide Complexes. The comproportionation reaction between 1 equiv of the previously reported complex (PNP^{OMe}-d_{12})$CrCl_3$ (**6**)[14] and 2 equiv of **4** in dichloromethane provides (PNP^{OMe}-d_{12})$CrPh_2Cl$ (**7**) as a dark olive-green powder in 71% isolated yield (eq 4). Slow diffusion of petroleum ether into a chlorobenzene solution of **7** at −35 °C provides X-ray quality crystals of this complex. The solid-state structure of **7** (Figure 3) reveals κ^3-(P,P,O) coordination of the PNP^{OMe} ligand with the chloride *trans* to the (P,O)-κ^2 chelating phosphorus. The chromium−oxygen bond length is 2.4371(14) Å, the chromium−phosphorus bond length for the (P,O)-κ^2 chelating phosphorus is 2.4414(6) Å, and the other chromium−phosphorus bond length is 2.6096(6) Å. The chromium−chloride bond length in **7** is 2.3078(6) Å, which is similar to the chromium−chloride bond length of 2.3210(7) Å observed for the chloride *trans* to the chelated phosphorus in **6**.[14]



(4)

Scheme 2



As with **4** and **5**, the room-temperature ^2H NMR spectrum of **7** in dichloromethane shows a single, very broad peak at $\delta = 6$ ppm. Cooling a dichloromethane solution of **7** displays two distinct coalescence points, both of which are between 0 and 25 °C. These higher temperature coalescence points indicate that the barriers for exchange processes for **7** are higher than those for **4**. The reasons for this difference are not immediately obvious, although the lower symmetry of **7** provides for five-coordinate intermediates of different energies, leading to a more complex free energy profile, possibly having some higher barriers.

By following the comproportionation reaction of **6** and **4** by ^2H NMR spectroscopy, intermediate formation of (PNP^{OMe}-d_{12})-$CrPhCl_2$ (**8**) may be observed. Complex **8** may be independently prepared by a comproportionation reaction between 2 equiv of **6** and 1 equiv of **4** in dichloromethane. **8** displays two separate ^2H NMR signals at room temperature at $\delta = 4.4$ ppm and $\delta = 11.8$ ppm in an approximate 1:1 ratio. An exchange process analogous to that proposed for **4** may again be invoked to explain the dynamic ^2H NMR behavior observed for **8**. The downfield peak observed at room temperature for **8** is assigned to the two methoxy groups that are exchanging for coordination to chromium, while the upfield peak is assigned to the two methoxy groups that exchange but are never coordinated to chromium. A coalescence point is observed at −65 °C; below this temperature the spectrum is unchanged, in accord with a static structure with one methoxy group coordinated to chromium, and exchange processes slow at these low temperatures.

Reactivity of 4 and 7: Trimerizations with (PNP)$CrPh_3$ and (PNP)$CrPh_2Cl$ as Precursors. Both **4** and **7** react with ethylene in toluene solution at room temperature over the course of hours to insert ethylene into their chromium−phenyl bonds and form styrene, ethylbenzene, 4-phenyl-1-butene, and higher ethylene insertion products, along with benzene. Formation of 1-hexene is not observed under these conditions.

Protonation of **4** and halide abstraction from **7** in toluene have been explored as possible routes to an ethylene trimerization catalyst system. Reactions of **4** with $[H(OEt_2)_2]^+\{B[C_6H_3(CF_3)_2]_4\}^-$ or **7** with $Na^+\{B[C_6H_3(CF_3)_2]_4\}^-$ in toluene at room temperature result in rapid formation of green solutions with an oily precipitate. Presumably, these reactions generate $[(PNP^{OMe}$-$d_{12})CrPh_2]^+B[C_6H_3(CF_3)_2]_4^-$ in both cases, either via protonation to liberate an equivalent of benzene or via halide abstraction to form NaCl, respectively (Scheme 2). After activation, formation of biphenyl by these systems proceeds, but does so very slowly; after 22 h less than 0.5 equiv of biphenyl is observed by GC-MS.

Protonation of **4** with $[H(OEt_2)_2]^+\{B[C_6H_3(CF_3)_2]_4\}^-$ in toluene or abstraction of chloride from **7** with $Na^+B[C_6H_3(CF_3)_2]_4^-$ in chlorobenzene, followed by exposure of the resulting mixture to an atmosphere of ethylene, yields active catalyst(s) for the trimerization of ethylene to 1-hexene (eq 5).

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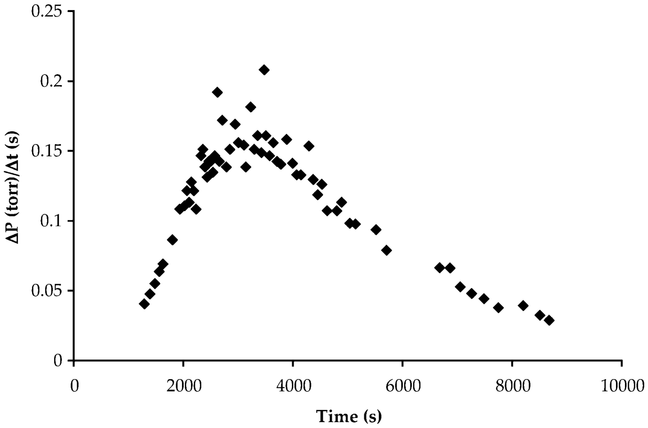
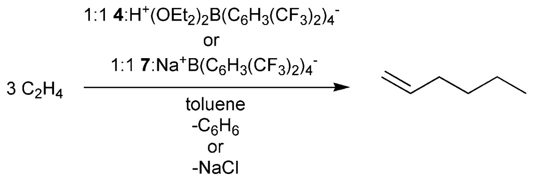


Figure 4. Ethylene consumption over time for trimerization catalyzed by **4**/$H^+(OEt_2)_2B[C_6H_3(CF_3)_2]_4^-$: 20 μmol of **4**, 20 μmol of $H^+(OEt_2)_2B[C_6H_3(CF_3)_2]_4^-$ in a mixture of 2 mL of Et_2O and 48 mL of toluene at room temperature; 1 atm of ethylene.

The structure in Scheme 2 with a κ^4-coordination of PNP is suggested on the basis of the normal preference for six coordination for chromium(III). Activation of complexes **4** and **7** provides a catalyst system that displays selectivity and activity similar to the $PNP^{OMe}/CrCl_3(THF)_3$/MAO system.[9] The difference in reactivity with ethylene observed for this activated, presumably cationic species versus the neutral precursors described above suggests that a cationic species with a weakly coordinating anion is necessary for catalytic activity. Preliminary experiments with $PNP^{SMe}/CrCl_3(THF)_3$/MAO indicate that **2** does *not* form a catalyst under the same conditions.



(5)

Although these catalysts are relatively well defined, there are some indications that the number of active chromium centers varies and that the catalyst is undergoing slow decomposition as it trimerizes ethylene. Activation of **4** with $[H(OEt_2)_2]^+\{B[C_6H_3(CF_3)_2]_4\}^-$ generates an ethylene trimerization catalyst with highly variable activity. Turnover numbers range from fewer than 10 mol to 2780 mol 1-hexene•mol^{-1} chromium. An examination of ethylene consumption over time for catalytic runs shows that the catalyst typically undergoes an initiation period, during which time ethylene consumption increases, followed by decomposition of the catalyst, as evidenced by a decrease in ethylene consumption over time. A representative plot of ethylene consumption over time for a typical trimerization run is shown in Figure 4. Plots of the natural log of the rate of ethylene consumption versus time during the decomposition period are linear, suggesting that catalyst decomposition is first-order in chromium (see the Supporting Information).

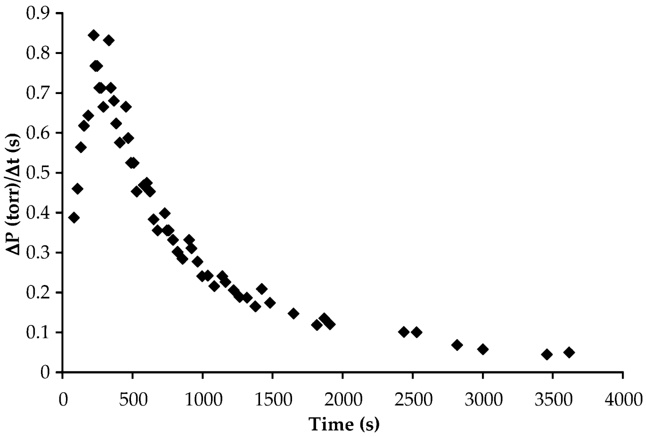


Figure 5. Ethylene consumption over time for the catalyst generated from **1** and $CrCl_3(THF)_3$ and activated by MAO after exposure to ethylene: 21 μmol of **1**, 21 μmol of $CrCl_3(THF)_3$, 6 mmol of MAO in 50 mL of toluene at room temperature; 1 atm of ethylene.

Treatment of **4** with either $[Me_2PhNH]^+\{B[C_6F_5]_4\}^-$ or MAO also generates an active ethylene trimerization catalyst. Reaction of **4** with $[Me_2PhNH]^+\{B[C_6F_5]_4\}^-$ (1 equiv) in a diethyl ether/toluene mixture provides a catalyst that achieves a final turnover number of 3050 mol 1-hexene•mol^{-1} chromium at 1 atm C_2H_4, which is the highest turnover number observed for the (PNP)-$CrPh_3$ system to date. By comparison, MAO activation (300 equiv) of **4** produces an active trimerization catalyst that gives an integrated 1500 mol 1-hexene•mol^{-1} chromium over the period of 1 h, after which point it is inactive for further ethylene consumption. Under these conditions the catalyst does not show an initiation period. Table 1 shows representative turnover numbers and catalyst lifetimes for a variety of catalytic runs.

Comparison to Trimerizations with $CrCl_3(THF)_3$/PNP/MAO. Trimerizations using $CrCl_3(THF)_3$/PNP/MAO (1:1:300) at 1 atm C_2H_4 give results similar to the better defined systems generated according to eq 5. MAO-generated catalysts display variable activities and undergo an initiation period followed by first-order decomposition. 1-Hexene turnovers range from 1700 to 4600. A representative plot of ethylene consumption over time for these catalysts is shown in Figure 5.

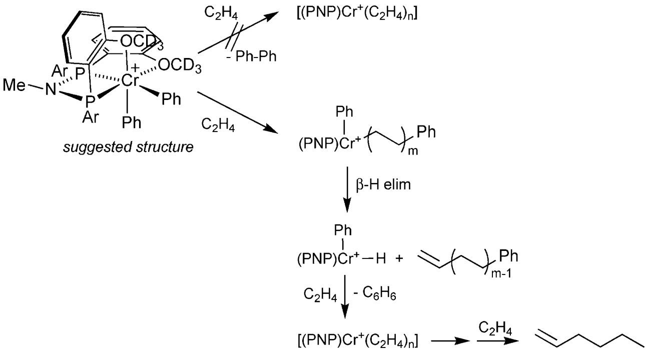
Initiation Mechanisms for 4 and 7. Possible initiation pathways for this family of catalysts were investigated by analyzing and quantifying the phenyl-containing organic products generated in trimerization reactions catalyzed by **4**/$[H(OEt_2)_2]^+\{B[C_6H_3(CF_3)_2]_4\}^-$ or **7**/$Na^+\{B[C_6H_3(CF_3)_2]_4\}^-$. Activations of **4** and **7** proceed rapidly to generate $[(PNP^{OMe}\text{-}d_{12})CrPh_2]^+\{B[C_6H_3(CF_3)_2]_4\}^-$ (vide supra). Once exposed to

Table 1. Representative Turnover Numbers and Approximate Catalyst Lifetimes for a Series of Ethylene Trimerization Runs with 4, 7, or $CrCl_3(THF)_3$/PNP as Catalyst Precursor

catalyst precursor	activator[a]	solvent	total turnover[b]	catalyst lifetime[c]
4	$[H(OEt_2)_2]^+[BAr^F_4]^-$	toluene	7	10
4	$[H(OEt_2)_2]^+[BAr^F_4]^-$	toluene/Et_2O	2780	>200
4	$[H(OEt_2)_2]^+[BAr^F_4]^-$	toluene/Et_2O	1790	180
4	$[H(OEt_2)_2]^+[BAr^F_4]^-$	chlorobenzene	735	90
4	$[Me_2PhNH]^+[B(C_6F_5)_4]^-$	toluene/Et_2O	3050	120
4	MAO	toluene	1490	65
7	$Na^+[BAr^F_4]^-$	chlorobenzene	450	
$CrCl_3(THF)_3/PNP^{OMe}$	MAO	toluene	2320	60
$CrCl_3(THF)_3/PNP^{OMe}$	MAO	toluene	4630	60

[a] $[BAr^F_4]^- = \{B[3,5\text{-}C_6H_3(CF_3)_2]_4\}^-$. [b] Mol 1-hexene/mol Cr. [c] Minutes.

Scheme 3



ethylene, this species may, among other possibilities, undergo reductive elimination of biphenyl or insertion of ethylene into a chromium−phenyl bond. In fact, only trace amounts of biphenyl are observed under trimerization conditions. Significantly, styrene and other phenyl-containing hydrocarbons are observed under trimerization conditions. Thus it appears that the chromium−phenyl bonds are cleaved primarily by ethylene insertion(s), which is eventually followed by β-hydrogen elimination and reductive elimination. The products are similar to those observed in the reaction of ethylene with the neutral species **4** and **7**. Some likely reaction pathways for the activated species are shown in Scheme 3. Although much more direct evidence remains to be gathered, the implications at this stage of the study are that the active catalyst is a cationic (PNP)-chromium species that shuttles between Cr^{III} and Cr^{I} with the PNP ligand utilizing the two phosphine donors and one or more methoxy ligands to stabilize the various intermediates along the catalytic cycle.

Conclusions

Phenyl chromium(III) complexes containing PNP ligands have been prepared and characterized both in the solid state and in solution. The triphenylchromium(III) complexes of two PNP ligands, ((PNP^{OMe}-d_{12})CrPh$_3$ (**4**) and ((PNP^{SMe}-d_{12})CrPh$_3$ (**5**), display octahedral geometries around chromium in the solid state; the PNP^{OMe} ligand coordinates to chromium with two phosphorus atoms and one oxygen, while the PNP^{SMe} coordinates through two sulfur atoms and one phosphorus. The X-ray and variable-temperature ^{2}H NMR data for **4** and **7** indicate a labile interaction between chromium and oxygen, which may be linked to catalyst activity and selectivity. We have proposed two distinct exchange processes in solution to explain the observed variable-temperature behavior.

Conversion of **4** or **7** to a [(PNP)Cr^{III}Ph$_2$]$^+$ cation by treatment with 1 equiv of acid or by precipitation of NaCl produces ethylene trimerization catalyst systems with selectivity and activity similar to the CrCl$_3$(THF)$_3$/PNP^{OMe}/MAO system, but that are much better defined in terms of the precatalyst structure. The behavior of this activated, cationic complex differs from that for the neutral triphenyl precursor with ethylene, in which 1-hexene is *not* formed, strongly suggesting that cationic complexes with noncoordinating anions are necessary for catalytic activity. Activities for these well-defined catalysts are variable, and in almost all cases a catalyst initiation period is followed by apparent first-order catalyst decomposition. Similar results have been obtained in attempts to reproduce the work reported by BP. Under trimerization conditions, chromium−phenyl bonds are cleaved by insertion(s) of ethylene, followed by β-hydrogen elimination and reductive elimination processes, to give phenyl-terminated ethylene oligomers and the active catalytic species.

Experimental Section

General Considerations. All air- and moisture-sensitive compounds were manipulated using standard vacuum line, Schlenk, or cannula techniques or in a glovebox under a nitrogen atmosphere, as described previously.[20] All gases were purified by passage over MnO on vermiculite and activated molecular sieves. Solvents were dried by the method of Grubbs.[21] Ethereal solvents were stored over sodium benzophenone ketyl, hydrocarbon solvents were stored over titanocene,[22] and halogenated solvents were dried over calcium hydride. Dichloromethane-d_2 was purchased from Cambridge Isotopes and distilled from calcium hydride. Methylaluminumoxane was purchased from Aldrich as a 10 wt % solution in toluene. $(CH_3)N(PCl_2)_2$,[23] PNP^{OMe}-d_{12} (**1**),[10] and (PNP^{OMe}-d_{12})CrCl$_3$ (**6**)[10] were prepared as previously described.

Instrumentation. All ^{1}H and ^{31}P NMR spectra were recorded on a Varian Mercury 300 spectrometer at 299.868 and 121.389 MHz, respectively, at room temperature unless indicated otherwise. All ^{2}H NMR spectra were recorded on a Varian INOVA 500 spectrometer at 76.848 MHz at room temperature unless indicated otherwise. All ^{1}H NMR chemical shifts are reported relative to TMS, and ^{1}H (residual) chemical shifts of the solvent are used as a secondary standard. ^{31}P NMR shifts are reported relative to an external H_3PO_4 standard. ^{2}H NMR chemical shifts are reported with respect to $CHDCl_2$ (natural abundance, 5.32 ppm) from the CH_2Cl_2 solvent or to an external D_2O reference (4.8 ppm). Temperatures of the NMR probe were calibrated using a methanol standard. EPR spectra were recorded on a Bruker EMX spectrometer. Elemental analysis was performed by Midwest MicroLab, LLC. GC measurements were taken on an Agilent 6890 Series GC using an Agilent HP-5 column. X-ray crystallography data were collected on a Bruker SMART 1000 ccd diffractometer.

PNP^{SMe}-d_{12} (2). A Schlenk flask was charged in the glovebox with magnesium turnings (1.474 g, 61 mmol, 1.24 equiv). On the vacuum line dry THF (100 mL) was added to the flask via vacuum transfer. Neat 2-bromothioanisole-d_3 (10.000 g, 49 mmol, 1 equiv) was added via syringe. The reaction mixture became warm upon addition and turned a pale brown color, and the reaction was left to stir at room temperature for 24 h. The Grignard solution was cannula transferred to a THF solution of $(CH_3)N(PCl_2)_2$ (2.626 g, 11 mmol, 0.22 equiv), which caused the solution to get warm, and the resulting yellow solution was stirred at room temperature for 1 week. THF solvent was removed in vacuo, and the product was isolated by recrystallization from a dichloromethane/methanol solvent mixture to obtain 1.598 g of **2** (22% yield). ^{1}H NMR (RT, 300 MHz, CDCl$_3$): δ 2.51 (t, 3H, Ar$_2$PN(CH_3)PAr$_2$), 7.06 (m, 8H, ArH), 7.32 (m, 8H, ArH). ^{31}P NMR (RT, 300 MHz, CDCl$_3$): δ 50 ppm (s, Ar$_2$$P$N(CH$_3$)$PAr_2$). ^{2}H NMR (RT, 500 MHz, CH$_2$Cl$_2$): δ 2.26 ppm (s, OCD_3).

(PNP^{OMe}-d_{12})CrPh$_3$ (4). In the glovebox, compound **1** (1.069 g, 2.01 mmol, 1.03 equiv) was dissolved in 75 mL of dichloromethane. Portions of CrPh$_3$(THF)$_3$ (0.974 g, 1.95 mmol, total, 1 equiv) were added as a slurry in tetrahydrofuran (approximately 2 mL) to the stirring solution of **1** over 5 min. The color of the reaction mixture turned deep red upon addition. Volatile materials were removed in vacuo, and approximately 50 mL of dichlo-

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romethane were added, followed by solvent removal in vacuo. The red solid residue was dissolved in approximately 25 mL of dichloromethane, and approximately 30 mL of petroleum ether were added to precipitate a red solid. This mixture was stored at −35 °C overnight. The solid material collected by filtration of the cold solution was recrystallized from a dichloromethane/petroleum ether mixture, collected on a sintered glass frit, and dried under vacuum to leave 1.050 g of **4** as a red, microcrystalline solid (66% yield). ^{2}H NMR (RT, 500 MHz, CH_2Cl_2): δ 8.47 ppm (s, OC*D*$_3$). Anal. Calcd for $C_{47}H_{34}D_{12}NO_4P_2Cr$: C, 69.26; H, 5.70; N, 1.72. Found: C, 69.03; H, 5.69; N, 1.86. $\mu_{eff} = 3.8\ \mu_B$. X-ray-quality crystals of **4** were obtained from slow diffusion of petroleum ether into a concentrated CH_2Cl_2 solution of the complex at −35 °C.

(PNP^{SMe}-*d*$_{12}$)CrPh$_3$ (5). Compound **5** was prepared from **2** (1.252 g, 2.10 mmol, 1 equiv) and **3** (1.050 g, 2.10 mmol, 1 equiv) using a procedure analogous to that used for compound **4**. An orange-brown solid was obtained, which was dissolved in approximately 25 mL of dichoromethane. Approximately 25 mL of petroleum ether were added to precipitate a brown powder. This mixture was stored at −35 °C overnight. The solid material collected by filtration of the cold solution was recrystallized from a dichloromethane/petroleum ether mixture, collected on a sintered glass frit, and dried under vacuum to leave 1.039 g of **5** as a brown solid (56% yield). ^{2}H NMR (RT, 500 MHz, CH_2Cl_2): δ −3.8 ppm (s, SC*D*$_3$). Anal. Calcd for $C_{47}H_{34}D_{12}NS_4P_2Cr$: C, 65.09; H, 5.36; N, 1.62. Found: C, 64.83; H, 5.35; N, 1.72. X-ray quality crystals of **5** were obtained from slow diffusion of petroleum ether into a concentrated CH_2Cl_2 solution of the complex at −35 °C.

(PNP^{OMe}-*d*$_{12}$)CrPh$_2$Cl (7). In the glovebox, solid **4** (0.517 g, 0.63 mmol, 2 equiv) and solid **6** (0.219 g, 0.32 mmol, 1 equiv) were placed in a 20 mL vial. Approximately 10 mL of CH_2Cl_2 was added to form a brown solution. The vial was wrapped in aluminum foil to protect it from light, and the reaction mixture was allowed to stir at room temperature for 2 h. The mixture turned a dark green color. Solvent was removed in vacuo to leave a green-brown powder, which was dissolved in approximately 10 mL of dichloromethane. Approximately 7 mL of petroleum ether were added to precipitate a green-brown solid. This mixture was stored at −35 °C overnight. The solid material was collected by filtration of the cold solution and then recrystallized from a dichloromethane/petroleum ether mixture, collected on a sintered glass frit, and dried under vacuum to leave 0.523 g of **7** as a green-brown powder (71% yield). ^{2}H NMR (RT, 500 MHz, CH_2Cl_2): δ 6 ppm (br s, OC*D*$_3$). Anal. Calcd for $C_{41}H_{29}D_{12}ClNO_4P_2Cr$: C, 64.69; H, 5.44; N, 1.84. Found: C, 64.87; H, 6.06; N, 1.65. X-ray quality crystals of **7** were obtained from slow diffusion of petroleum ether into a concentrated chlorobenzene solution of the complex at −35 °C.

(PNP^{OMe}-*d*$_{12}$)CrPhCl$_2$ (8). Solid **4** (0.014 g, 0.017 mmol, 1 equiv) and solid **6** (0.024 g, 0.035 mmol, 2 equiv) were placed in a 20 mL vial, and approximately 2 mL of dichloromethane was added. The vial was wrapped in aluminum foil to protect it from light and left to stir at room temperature for 12 h. The solution turned a dark green color. ^{2}H NMR (RT, 500 MHz, CH_2Cl_2): δ 4.4 ppm (s, 6D, OC*D*$_3$), 11.8 ppm (s, 6D, OC*D*$_3$).

General Procedure for Trimerization of C_2H_4 with 4/[H(Et$_2$O)$_2$]$^+${B[C$_6$H$_3$(CF$_3$)$_2$]$_4$}$^-$. In the glovebox a 250 mL round-bottom flask was charged with **4** (0.016 g, 0.020 mmol, 1 equiv) and $[H(Et_2O)_2]^+\{B[C_6H_3(CF_3)_2]_4\}^-$ (0.020 g, 0.020 mmol, 1 equiv), and approximately 2 mL of diethyl ether followed by 48 mL of toluene were added to give a pale green solution. The flask was equipped with a 180° needle valve, degassed on the vacuum line at −78 °C, warmed to room temperature, and backfilled with 1 atm of ethylene. Ethylene consumption was monitored using a mercury manometer. After 1 h the reaction was quenched with H_2O. The organic fraction was separated and passed through a plug of activated alumina to remove any chromium compounds, and this mixture was analyzed by GC and GC-MS. 1-Hexene was quantified by comparison to a mesitylene standard, which was added to the reaction mixture. The reaction produces 1-hexene with a range of 10−3000 turnovers in greater than 85% overall selectivity. A similar procedure was followed in the case of activation of **4** with $[Me_2PhNH]^+\{B[C_6F_5]_4\}^-$ or MAO.

General Procedure for Trimerization of C_2H_4 with 7/Na$^+${B[C$_6$H$_3$(CF$_3$)$_2$]$_4$}$^-$. In the glovebox a 250 mL round-bottom flask was charged with **7** (0.017 g, 0.022 mmol, 1 equiv) and $Na^+\{B[C_6H_3(CF_3)_2]_4\}^-$ (0.021 g, 0.024 mmol, 1.1 equiv) and equipped with a 180° needle valve. The flask was attached to the vacuum line, and approximately 50 mL of chlorobenzene was added via vacuum transfer. The flask was backfilled with 1 atm of ethylene, and the mixture was allowed to warm to room temperature and stir while open to an ethylene atmosphere. A pale green solution was formed as the mixture melted, and the reaction was stirred for 20 min to 1.5 h, at which point it was quenched with H_2O. The organic fraction was separated and filtered through a plug of activated alumina to remove any chromium, and this mixture was analyzed by GC and GC-MS. The reaction produces 1-hexene with a range of 300−1000 turnovers in greater than 85% overall selectivity.

General Procedure for Trimerization of C_2H_4 with CrCl$_3$(THF)$_3$/PNP^{OMe}/ MAO. In the glovebox a 250 mL round-bottom flask was charged with **1** (0.011 g, 0.021 mmol, 1 equiv) and $CrCl_3(THF)_3$ (0.008 g, 0.021 mmol, 1 equiv), 50 mL of toluene was added, and the flask was equipped with a 180° needle valve. The apparatus was attached to the high-vacuum line, degassed at −78 °C, and backfilled with 1 atm of ethylene. After the solution had warmed to room temperature, MAO solution (3.481 g, 10 wt % in toluene, 6 mmol, 300 equiv) was added via syringe under a positive ethylene flow. Ethylene consumption was monitored using a mercury manometer. After 1 h the reaction was quenched with H_2O. The organic fraction was separated and passed through a plug of activated alumina to remove any chromium compounds, and this mixture was analyzed by GC and GC-MS. The reaction produces 1-hexene with a range of 1000−4700 turnovers in greater than 85% overall selectivity.

Acknowledgment. We thank Dr. Steven A. Cohen for helpful discussions. We are grateful to BP Chemicals (now Innovene) for financial support.

Supporting Information Available: Tables of bond lengths, angles, and anisotropic displacement parameters for **7** (corresponding tables for **4** were reported previously).[13] Drawing of solid-state structure of **5**. EPR spectra of **4** and **5**. Plots of the natural log of ethylene consumption versus time with various catalytic systems. X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

OM0506062