Unusual Ligand Transformation Mediated by Chromium(III): Hydrolytic Disintegration of a [PNP] Hybrid Ligand with CH_3CN Insertion

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Concomitant reaction among coordinated CH_3CN and a bidentate [P(N)P] aminodiphosphine ligand in $[Ph_2PN(R)PPh_2]CrCl_3(CH_3CN)$ (R = Cy, Ph) with H_2O results in a tridentate [ONO] amino-α-diphosphoryl ligand in $[Ph_2P(O)C(CH_3)(NH_2)P(O)Ph_2]CrCl_3$. The latter releases the free ligand upon treatment with excess water or gives a cationic complex, $\{[Ph_2P(O)C(CH_3)(NH_2)P(O)Ph_2]CrCl_2[P(O)(H)Ph_2]\}^+SbF_6^-$, when treated with $AgSbF_6$. All the new compounds have been crystallographically established. The catalytic activities of these complexes toward ethylene oligomerization and polymerization are described and compared.

Introduction

Bi- and multidentate hybrid ligands are ligands of choice in Cr(III)-catalyzed ethylene oligomerization.[1] The aminodiphosphines $RN[(CH_2)_nPR'_2]_2$ ($n \geq 0$) (PNP) are typical examples of such ligands.[2] They offer excellent support to the metal center by balancing the key chemical stability, catalytic activity, and site selectivity.[3] Their uses also allow modification of the donor characteristics, ligand substituents, and skeletal backbone. Modification of such hybrid ligands provides a systematic means to tune the electronic and steric features of the precatalyst. This approach to catalyst design is complemented by ongoing vigorous mechanistic research in olefin oligomerization. Current knowledge points to a metallacyclic pathway involving coordinatively unsaturated intermediates and perhaps a reversible Cr(I)/Cr(III) process.[4] If the hybrid character of the multidentate ligand is expressed in terms of a dynamic formation and cleavage of the M−L bond, the resultant hemilability could offer additional stabilization to the unsaturated intermediate.[5] Our recent isolation of $CrCl_3(CH_3CN)(PNP)$,[6] which catalyzes ethylene polymerization, is an illustration of this model. It is formed directly from ligand addition to $CrCl_3(THF)_3$ possibly via a saturated dinuclear species $Cr_2Cl_4(\mu\text{-}Cl)_2(PNP)_2$.[3c] This mononuclear $CrCl_3(CH_3CN)(PNP)$ is a 15-electron complex and would be 13-electron, five-coordinate, and heavily unsaturated without the solvate (CH_3CN) or ligation from the internal donor (i.e., N) of the hybrid ligand. Coordination of CH_3CN therefore provides a simple model for the access of a range of potentially unsaturated and catalytically active Cr(III) complexes supported by the hybrid ligand. This type of catalyst in olefin oligomerization and polymerization has many advantages. We herein report an unexpected complication that could lead to catalyst degradation. It arises from the unusual metal-mediated ligand interaction between the PNP ligand and solvate, viz., CH_3CN. This results in an hitherto unknown ligand transformation and formation of a new α-aminophosphine oxide type of ligand,[7] thus turning a PNP into an ONO-type of ligand in a single step. To our knowledge, such interligand interaction and transformations are unprecedented.

Results and Discussion

Synthesis and Structures. The PNP ligands with Cr precursors and their related dinuclear Cr(III) PNP complexes $\{[Ph_2PN(R)PPh_2]CrCl_2(\mu_2\text{-}Cl)]\}_2$ (**1**) developed by Bollmann et al.[3a] are active ethylene tetramerization catalysts. In a coordinating solvent such as CH_3CN, the Cr(III) complex **1** dissolves but also undergoes Cr−Cl−Cr bridge cleavage to form a solvate-

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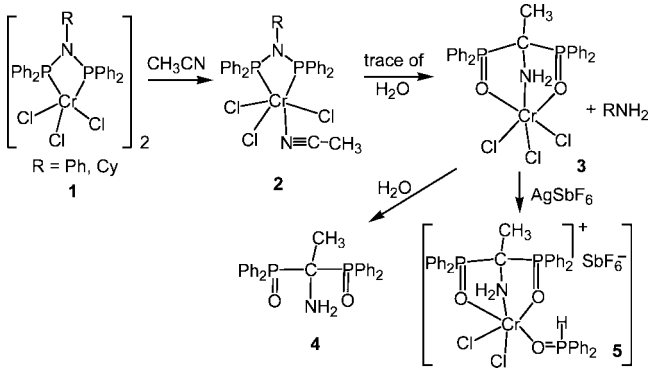
Scheme 1



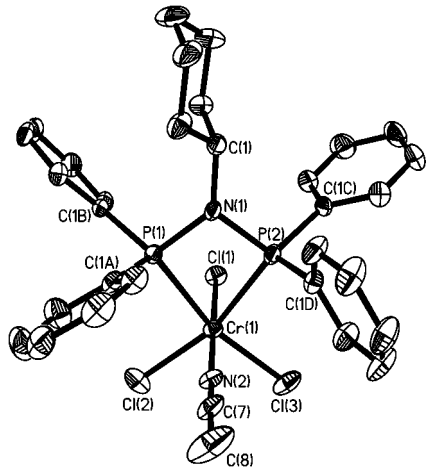


Figure 1. ORTEP diagram of complex **2** (R = Cy) with thermal ellipsoids at the 40% probability level. Hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of Complexes 2 and 3

	2	3
Cr(1)−P(1)	2.4887(13)	
Cr(1)−P(2)	2.4850(13)	
Cr(1)−N(1)	2.051(4)	2.141(7)
Cr(1)−Cl(1)	2.2780(12)	2.307(3)
Cr(1)−Cl(2)	2.2995(14)	2.278(3)
Cr(1)−Cl(3)	2.2953(13)	2.313(3)
Cr(1)−O(1)		2.039(6)
Cr(1)−O(2)		2.003(6)
C(1)−C(2)		1.511(11)
N(1)−C(1)	1.501(5)	1.523(10)
P(1)−O(1)		1.521(6)
P(2)−O(2)		1.505(6)
P(1)−N(1)−P(2)	104.74(18)	
P(1)−Cr(1)−P(2)	65.95(4)	
P(1)−C(1)−P(2)		109.3(4)
O(1)−Cr(1)−O(2)		87.7(2)

stabilized mononuclear complex, $[Ph_2PN(R)PPh_2]CrCl_3(CH_3CN)$ (**2**), Scheme 1.

The solid state three-dimensional structure of **2** (R = cyclohexyl) was established using X-ray crystallography (Figure 1 and Table 1). The related analogue with R = $CH_3-S-C_3H_6-$ has been reported earlier.[6] Complex **2** is a six-coordinated complex with a P,P′-bidentate [PNP] ligand with a spectating amine but coordinated CH_3CN. It is stable in pure and dry CH_3CN, but in the presence of trace H_2O, the [PNP] ligand breaks down and transforms to a new class of tridentate [ONO] hybrid ligand in $[Ph_2P(O)C(CH_3)(NH_2)P(O)Ph_2]CrCl_3$ (**3**). IR analysis indicates the loss of the nitrile function. The presence

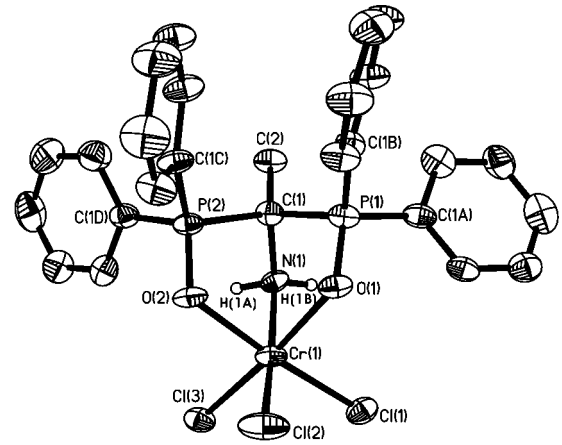


Figure 2. ORTEP diagram of complex **3** with thermal ellipsoids at the 40% probability level.

of ν_{N-H} at 3082 and 3058 cm^{-1} is in agreement with the formation of a new $-NH_2$ function.

Structural confirmation of complex **3** comes from single-crystal X-ray diffraction studies (Figure. 2 and Table 1). It has a distorted octahedral geometry with a *fac*-$[CrCl_3]$ core completed by [ONO] tridentate coordination. The Cr−O lengths (2.003(6) and 2.039(6) Å) are significantly shorter than that of the related PNP complex $CrCl_3\{[\eta^3\text{-}(P,P,O)\text{-}(PNP^{OMe})]\}$ with an "agostic" Cr−O interaction (2.1562(15) Å).[8] The Cr−N bond (2.141(7) Å) is comparable to those in the trimerization catalysts, viz., $CrCl_3[HN(CH_2CH_2PPh_2)_2]$ (2.137(3) Å)[9] and $CrCl_3[HN(CH_2CH_2SEt)_2]$ (2.1059(18) Å).[10] This hybrid tridentate [ONO] ligand coordinates to a *fac*-Cr(III) core with two fused five-membered rings such that two phenyl groups across the two rings are oriented face-to-face with some degree of $\pi\cdots\pi$ stacking (interplanar distance = 3.52 Å).

In a single reaction, a bidentate [P(N)P] aminodiphosphine remarkably transforms to a tridentate [ONO] amino-α-diphosphoryl ligand. This is driven by the favorable conversion of the reactive $[CrCl_3L_2(solvate)]$ to the stable $[CrCl_3(L_2L')]$ core with extrusion of free amine RNH_2. To our knowledge, there is no precedent of such ligand transformation. A possible pathway is the hydro-heterolytic cleavage of the reactive $P^{III}-N$ bonds in **2**, followed by CH_3CN insertion into the void between the two phosphoryl functions (**A**), resulting in proton and electron transfer (**B**) to create the macrocyclic ligand (**3**), Scheme 2. Effectively, the first step is ligand dissection, whereas the second is a ligand reconstruction step.

This ligand transformation has several favorable driving forces. A strained four-membered ring is replaced by the more stable fused five-membered rings with additional macrocyclic effect. The reactive (P(1)−Cr(1)−P(2) 65.95(4)°) P−N bonds are replaced by the more robust C−P and C−N with additional P−O bonds. Removal of the labile CH_3CN and ejection of stable amine RNH_2 also contribute to the thermodynamic drive.

The potential use of this ligand transformation as a synthetic method for new [ONO] ligand $Ph_2P(O)C(CH_3)(NH_2)P(O)Ph_2$ (**4**) is demonstrated in the hydrolytic reaction of **3**. In the presence of excess H_2O, complex **3** breaks down to release the [NON] ligand **4** (65% yield), which has been spectroscopically

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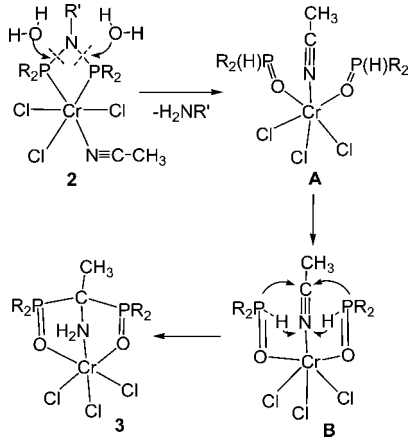
Scheme 2. Proposed Conversion Pathway to 2 to 3



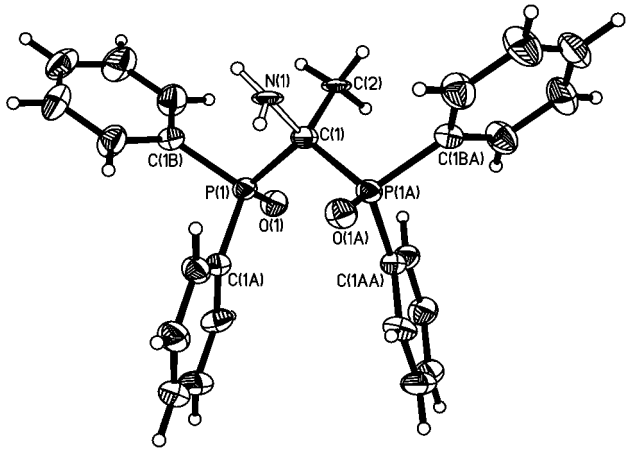


Figure 3. ORTEP diagram of complex **4** with thermal ellipsoids at the 40% probability level. Selected bond lengths [Å] and bond angles [deg]: P(1)−O(1) 1.490(3), P(1)−C(1) 1.879(3), C(1)−N(1) 1.476(11), O(1)−P(1)−C(1) 112.47(12), N(1)−C(1)−C(2) 107.4(5), N(1)−C(1)−P(1) 112.6(4), C(2)−C(1)−P(1) 107.6(4).

and crystallographically established (Scheme 1). The dihedral angle between the O(1)−P(1)−C(1) and P(1)−C(1)−P(1A) planes expands beyond perpendicular, viz., 113.7(3)°. The anti-orientation of the two P═O bonds moves the phenyl rings away from each other and removes the π stacking seen in the complexed state (**3**).

In the absence of Cr, the free [PNP] ligand $Ph_2PN(Ph)PPh_2$ in CH_3CN can react with excess water (>1000 fold) to give **4** but only very slowly (~30 days), with much lower yield (ca. 20%) and also giving another unidentified byproduct. There is no evidence of the formation of **4** when the PNP ligand is added to a stoichiometric mix of CH_3CN and water under ambient conditions, even after prolonged stirring of >30 days.

Compounds with the P−C(N)−P functions have been shown to be biologically active.[11] For example, α-aminophosphates can mimic the action of natural amino acids and act as enzyme inhibitors.[11a] However, only a few methods of their preparation are known.[12] This metal-mediated pathway could provide a new alternative one-step methodology to amino-diphosphine oxides and diphosphonates such as $R_2P(O)-C(NH_2)-R'-P(O)R_2$ under ambient conditions. Attempts to develop the use of Cr catalysts to promote the hydrolysis of PNP compounds to form new amino-diphosphonates are currently in progress.

Chloride abstraction reaction of **3** with $AgSbF_6$ in CH_3CN was successful but did not give the expected product $[\{Ph_2P(O)C(CH_3)(NH_2)P(O)Ph_2\}CrCl_2(CH_3CN)]^+$; presumably the $[Cr^{III}Cl_2(solvate)]$ core is too reactive to be isolated. Its formation triggers a ligand cleavage to release Ph_2POH, which subsequently attacks the intermediate to yield $\{[Ph_2P(O)C(CH_3)(NH_2)P(O)Ph_2]CrCl_2[P(O)(H)Ph_2]\}^+SbF_6^-$ (**5**) (Scheme 1). Other decomposition byproducts are not isolated or identified. The structure of **5** has been confirmed by X-ray single-crystal crystallographic analysis, but the quality of data is too poor to justify any meaningful structural discussions.

Ethylene Oligomerization and Polymerization. Typical ONO ligands, represented by amine bis(phenolate), *N*-alkoxy-β-ketoiminate, and Schiff base, have shown good catalytic activity in the polymerization of alkenes and enantioselective catalysis.[13] However, we are not aware of any report on metal complexes with the [ONO] donor set on a P−C−P backbone. The ethylene oligomerization activities of **2**−**5** were investigated in toluene with MAO as coactivator (Table 2). Preliminary data collected at rt under 430 psi pressure of ethylene with a [Al]/[Cr] ratio of 420 indicated low to moderate activities (1300−13 700 g prod./g Cr) of **2**−**5** toward oligomerization and polymerization (Table 2).

The catalytic activities are significantly influenced by the ligand environment. The combination of Cr(III) with the hybrid ligand is essential to achieve ethylene oligomerization and polymerization and influence their distribution as well as the α-alkene selectivity. Without these ligands, Cr precursors such as $Cr(acac)_3$ and $CrCl_3(THF)_3$ give little or no oligomers. They give polymers but with mediocre activities (Table 2, entries 3 and 5). While Cr-PNP complexes are reported to be excellent in selective ethylene trimerization and tetramerization,[3] the introduction of MeCN into the Cr-PNP coordination sphere (giving precatalyst **2**) will drastically alter the selectivity to exclusive production of polyethylene (PE) with an activity of 13 700 g prod./g Cr when dry toluene is used as solvent (Table 2, entry 1). The role of CH_3CN is unclear, but it could stabilize the metallacyclic intermediates[8,14] by suppressing the β-hydrogen elimination and therefore encourage growth of the metallacyclic ring. The catalytic activity and production of PE decrease significantly when the bidentate PNP-Cr precatalyst **2** is replaced by the tridentate ONO-Cr complex **3** and a crude form of **5** (1300 and 4500 g prod./g Cr, respectively) (Table 2, entries 2 and 7). A tentative comparison between a neutral (**3**) and ionic complex **5** of similar makeup of hybrid ligands shows similar activities toward oligomerizations, but **5** shows an at least 7-fold increase compared to **3** in terms of PE activity. These data should be treated with caution since **5** is invariably contaminated by other unknown impurities. In general both

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Table 2. Activities and Selectivities of Different Catalytic Systems toward Polymerization and Oligomerization of Ethylene[a]

						oligomer distribution (wt %)				
entry	catalyst	activity[b]	total product (mg)	PE (%)[c]	oligomers (%)	$C_4(\alpha\text{-}C_4)$	$C_6(\alpha\text{-}C_6)$	$C_8(\alpha\text{-}C_8)$	$C_{10}(\alpha\text{-}C_{10})$	C_{12+}
1	**2** (R = Cy)	13700	286	100	0					
2	**3**	1300	28	86	14	76 (83)	0	2 (43)	7 (42)	19
3	$Cr(THF)_3Cl_3$	600	13	100	0					
4[d]	**4**/$Cr(THF)_3Cl_3$	2500	52	100	0					
5	$Cr(acac)_3$	1500	32	94	6	3 (60)	8 (40)	2 (45)	11 (42)	76
6[d]	**4**/$Cr(acac)_3$	7400	154	10	90	8 (43)	15 (73)	13 (72)	21 (60)	43
7	**5**	4500	94	84	16	70 (14)	0	18 (26)	0	12
8[e]	**5**	12 300	255	96	4	0	0	0	0	100

[a] Conditions: 0.4 μmol of Cr loading, toluene, 430 psi of ethylene, 420 equiv of MAO, room temperature, 1 h. Average at least 3 runs. [b] Activity = g prod./g Cr. [c] % = weight %. [d] 0.4 μmol of **4** is used. [e] Chlorobenzene is used as solvent instead of toluene.

complexes are not very active, probably because of their low solubility in the reaction solvent, toluene. When it is replaced by a more polar solvent such as chlorobenzene, in which **5** is significantly more soluble, the PE activity improves by nearly 2-fold to 12 300 g/g (Table 2, entry 8). Attempts to characterize the polymer product by GPC analysis were not successful, as it is insoluble under standard analytical procedure (PE dissolution in 1,3,5-trichlorobenzene at 145 °C). This polymer product is likely to be high-density polyethylene (HDPE).[15]

The nature of the metal complex also influences the oligomeric selectivity. Although the ONO ligand **4** with $CrCl_3(THF)_3$ catalyzes ethylene polymerization (entry 4), it works with $Cr(acac)_3$ to promote good activity (7400 g prod./g Cr) toward ethylene oligomerization in which the distribution of the liquid products (C_4-C_{20}) (entry 6) follows a typical Schulz−Flory distribution with a K value of 0.82.[16] Activation of the **4**/$Cr(acac)_3$ system with other Lewis acid cocatalysts such as $EtAlCl_2$, $AlMe_3$, and BEt_3 or variation of the ethylene pressure will affect the overall catalytic activity but not the oligomer distribution. At higher temperatures (up to 80 °C), the activity increases by 2-fold, but the selectivity favors PE over oligomers, with the latter production greatly reduced to 15%.

Conclusion

We have demonstrated an unusual ligand destruction followed by reconstruction process during which the ligand is reconfigured from a bidentate [PNP] to a tridentate [ONO] donor set. As this transformation is facilitated by coordinated CH_3CN and water, it implies that in principle all P−X−P (X = N, O, Si, S, etc.) hybrid ligands with reactive X−P bonds currently used in ethylene oligomerization are potentially vulnerable to such hydro-heterolytic cleavage, and hence such catalytic reactions could not be used in CH_3CN solvent, especially when strict exclusion of H_2O is difficult. This serendipitous discovery has revealed a direct pathway to prepare a new type of catalytically active hybrid ligand. It also prompted us to design a new generation of ligands that can support Cr(III) in olefin oligo- and polymerization in more polar solvents such as nitriles and alcohols.

Experimental Section

General Comments. All reactions were carried out using conventional Schlenk techniques under an inert atmosphere of nitrogen or argon with an M. Braun Labmaster 130 inert gas system. NMR spectra were measured on Bruker ACF300 300 MHz FT NMR spectrometers (^1H at 300.14 MHz, ^{13}C at 75.43 MHz, and ^{31}P at 121.49 MHz). Mass spectra were obtained on a Finnigan Mat 95XL-T spectrometer. Elemental analyses were performed by the microanalytical laboratory in-house. All chemicals were obtained from Sigma-Aldrich or Strem Chemicals unless stated otherwise. $\{[Ph_2PN(Cy)PPh_2]CrCl_3\}_2$, $Ph_2PN(Cy)PPh_2$, and $Ph_2PN(Ph)PPh_2$ were prepared with modifications of literature procedures.[3a] In all the examples, the molar mass of methylaluminoxane (MAO) (10 wt % in toluene solution) was taken to be 58.016 g/mol, corresponding to the (CH_3-Al-O) unit, in order to calculate the molar quantities of MAO used in the preparation of the catalysts described below.

Synthesis of $[Ph_2PN(Cy)PPh_2]CrCl_3(CH_3CN)$ (2). To the solid of $\{[Ph_2PN(Cy)PPh_2]CrCl_3\}_2$ (81 mg, 0.13 mmol) in a test tube was added CH_3CN (1 mL) to give rapid precipitation of blue crystals of **2**. The solution was kept at −30 °C for 1 day to maximize the crystal deposit. After removing the mother liquid, the crystals were collected and washed by hexane and dried under vacuum. Yield: 41 mg, 48%. MS (FAB^+): m/z 589 $[M - Cl - CH_3CN]^+$, 554 $[M - 2Cl - CH_3CN]^+$, 468 $[Ph_2PN(Cy)PPh_2]^+$, 384 $[Ph_2PNPPh_2]^+$, 185 $[PPh_2]^+$. Anal. (%) Calcd for $C_{32}H_{34}N_2P_2CrCl_3$: C 57.63, H 5.14, N 4.20. Found: C 56.26, H 4.94, N 4.53.

One-Pot Synthesis of $[Ph_2P(O)C(CH_3)(NH_2)P(O)Ph_2]CrCl_3$ (3). Method A: To a solution of $Ph_2PN(Cy)PPh_2$ (1.13 g, 2.42 mmol) in CH_2Cl_2 (5 mL) was added $CrCl_3(THF)_3$ (0.906 g, 2.42 mmol) and the mixture stirred at rt for 30 min to give a green solution. The solvent was removed *in vacuo*. The dark green solid obtained was dissolved in CH_3CN to give a dark blue solution of **2**. Water (0.1 mL) was then added to the solution and the mixture kept at rt for 10 days to give crystalline purple deposits of **3**. The mother liquor was decanted and the solid product collected and dried *in vacuo* [yield: 0.767 g, 53% based on $CrCl_3(THF)_3$].

Method B: A procedure similar to method A, using $Ph_2PN(Ph)PPh_2$ instead of $Ph_2PN(Cy)PPh_2$, yielded **3** [yield: 82.9 mg, 57% based on $CrCl_3(THF)_3$].

Method C: **2** (0.237 g, 0.36 mmol) was dissolved in MeCN and H_2O (15 μL) was injected. The reaction mixture was stirred for 7 days under nitrogen and left to stand overnight before the mother liquor was decanted. The purple solid obtained was dried *in vacuo* [yield: 0.208 g, 96%].

Data for **3**: IR [Nujol, cm^{-1}]: ν(N−H) 3082 m, 3058 m. MS (FAB^+): m/z 567 $[M - Cl]^+$, 532 $[M - 2Cl]^+$, 185 $[PPh_2]^+$. Anal. (%) Calcd for $C_{26}H_{25}NP_2O_2CrCl_3 \cdot H_2O$: C 50.22, H 4.38, N 2.25. Found: C 50.28, H 4.46, N 2.30.

Synthesis of $Ph_2P(O)C(CH_3)(NH_2)P(O)Ph_2$ (4). Purple, solid **3** (180 mg, 0.298 mmol) was suspended in water (10 mL) and kept for 2 days until a crystalline white product of **4** was precipitated. The solid was collected, washed with cold water, then dissolved in toluene, filtered through a layer of Celite, and dried over anhydrous $MgSO_4$. The mixture was then filtered and the solvent evaporated carefully to give a solid, which was collected and dried *in vacuo*. Yield: 87 mg (65%). IR [Nujol, cm^{-1}]: ν(N−H) 3065 w. ^1H NMR ($CDCl_3$): δ 8.10 (s, 4 H, Ph), 7.98 (s, 4 H, Ph), 7.40−7.31 (m, 12

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Table 3. Crystal Data and Structure Refinement Parameters for Complexes 2, 3, and 4

	2	3	4
empirical formula	$C_{32}H_{34}Cl_3CrN_2P_2$	$C_{54}H_{53}Cl_6Cr_2N_3O_6P_4$	$C_{26}H_{25}NO_2P_2$
M_r	666.90	1280.57	445.41
temp, K	223(2)	223(2)	223 (2)
cryst color	blue	purple	colorless
cryst size, mm^3	0.20 × 0.08 × 0.06	0.10 × 0.08 × 0.06	0.26 × 0.20 × 0.14
cryst syst	orthorhombic	monoclinic	monoclinic
space group	*Pbca*	*P*2(1)/*c*	*C*2/*c*
a, Å	10.8132(9)	20.8878(15)	20.424(15)
b, Å	17.3988(13)	18.7658(14)	8.974(7)
c, Å	34.178(3)	15.4625(10)	12.342(9)
α, deg	90	90	90
β, deg	90	110.622(2)	99.544(15)
γ, deg	90	90	90
V, Å^3	6430.1(9)	5672.6(7)	2231(3)
Z	8	4	4
density, Mg/m^3	1.378	1.499	1.326
abs coeff, mm^{-1}	0.729	0.830	0.219
F(000)	2760	2624	936
θ range for data collection, deg	2.23 to 25.00	1.04 to 25.00	2.02 to 27.50
index ranges	$-12 \le h \le 12$, $-20 \le k \le 19$, $-40 \le l \le 35$	$-24 \le h \le 23$, $-22 \le k \le 21$, $-18 \le l \le 17$	$-26 \le h \le 26$, $-5 \le k \le 11$, $-16 \le l \le 15$
no. of reflns collected	35 585	32 273	7201
no. of indep reflns	5666 (R_{int} = 0.1468)	9999 (R_{int} = 0.1160)	2551 (R_{int} = 0.0751)
max. and min. transmn	0.9575 and 0.8678	0.9519 and 0.9216	0.9700 and 0.9453
no. of data/restraints/params	5666/0/362	9999/4/689	2551/21/151
final *R* indices [$I > 2\sigma(I)$][ab]	R1 = 0.0626, wR2 = 0.1120	R1 = 0.1034, wR2 = 0.2122	R1 = 0.0827, wR2 = 0.2262
R indices (all data)	R1 = 0.1026, wR2 = 0.1243	R1 = 0.1626, wR2 = 0.2383	R1 = 0.1079, wR2 = 0.2453
goodness-of-fit on F^2[c]	1.032	1.091	1.068
large diff peak and hole, e Å^{-3}	0.357 and −0.326	1.054 and −0.877	0.871 and −0.459

[a] $R = (\sum||F_o| - |F_c||)\sum|F_o|$. [b] $wR_2 = [(\sum w|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [c] GoF = $[(\sum w|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

H, Ph), 2.13 (t, J = 10.7 Hz, 2 H, NH_2), 1.39 (t, J = 15.5 Hz, 3 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 132.6 (t, J = 4.4 Hz, Ph), 132.2 (t, J = 4.4 Hz, Ph), 131.7 (s, Ph), 131.3 (s), 128.0 (q, J = 5.5 Hz, Ph), 58.1 (t, J = 66.4 Hz, $C(CH_3)(NH_2)$), 21.8 (s, CH_3). ^{31}P NMR ($CDCl_3$): δ 32.66. MS (FAB$^+$): *m*/*z* 446 [M + H]$^+$, 244 $[(Ph_2P(O)C(CH_3)(NH_2)]^+$, 185 $[PPh_2]^+$. Anal. (%) Calcd for $C_{26}H_{25}NP_2O_2$: C 70.11, H 5.61, N 3.14. Found: C 69.77, H 5.80, N 2.77.

Synthesis of {[$Ph_2P(O)C(CH_3)(NH_2)P(O)Ph_2$]$CrCl_2$[P(O)(H)$Ph_2$]}$^+SbF_6^-$ (5). To a suspension of **3** (25 mg, 0.042 mmol) in CH_3CN (4 mL) was added $AgSbF_6$ (14 mg, 0.042 mmol), and the mixture was stirred at rt for 24 h. The resultant cloudy solution was filtered through a layer of Celite to give a green solution. The volatile materials were removed *in vacuo*. The green residue was redissolved in CH_3CN and filtered. Et_2O was carefully added and the mixture left upon standing at −30 °C for a few weeks to give dark green crystals of **5**. Yield: ca. 12 mg (29%). IR [Nujol, cm^{-1}]: *ν*(N−H)3065w.MS(FAB$^+$):*m*/*z*769{[$Ph_2P(O)C(CH_3)(NH_2)P(O)Ph_2$]$CrCl_2$[P(O)(H)$Ph_2$]}$^+$, 567 [($Ph_2P(O)C(CH_3)(NH_2)P(O)Ph_2$)$CrCl_2$]$^+$, 532 [($Ph_2P(O)C(CH_3)(NH_2)P(O)Ph_2$)CrCl]$^+$. MS (FAB$^-$): *m*/*z* 236 $(SbF_6)^-$. This compound was inevitably contaminated by other Cr impurities, and hence satisfactory elemental analysis could not be obtained.

Oligomerization of Ethylene. The catalytic activities were screened by an Endeavor parallel pressure reactor, following recommended procedures.[6] At the end of each experiment, the vessels were cooled to ambient temperature and depressurized. The reaction mixture was cooled to 0 °C and terminated by addition of 10% aqueous HCl. A small sample of the upper-layer solution was filtered through a layer of Celite and analyzed by GC. The individual products of oligomerization were identified by GC-MS. The remainder of the upper-layer solution was filtered to isolate the solid polymeric products. The solid products were suspended in 10% aqueous HCl and stirred for 24 h, dried under reduced pressure, and weighed. The results are summarized in Table 2.

Crystal Structure Analyses. Diffraction-quality single crystals were mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector, using Mo Kα radiation (*λ* 0.71073 Å). The data were corrected for Lorentz and polarization effects with the SMART suite of programs[17] and for absorption effects with SADABS.[18] Structure solution and refinement were carried out with the SHELXTL suite of programs.[19] The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. The asymmetric unit in **3** contains two molecules of the complex [$Ph_2P(O)C(CH_3)(NH_2)P(O)Ph_2$]$CrCl_3$ and one solvent acetonitrile, as well as two water molecules. The hydrogen atoms of the two water molecules were not located due to poor data quality. The final *R* values are R_1 = 0.103 and wR_2 = 0.2365 These relatively high values could be caused by the poor quality of the crystal (R_{int} = 0.116). Other features including the thermal parameters of the atoms are normal. In **4**, the asymmetric unit contains half a molecule. The molecule was generated by the 2-fold symmetry. The expected molecule $(Ph_2PO)_2C(CH_3)(NH_2)$, as evident by chemical and NMR analysis, actually does not have 2-fold symmetry. The only reasonable possibility is disorder of CH_3 and NH_2 groups with 50:50 occupancies. Use of space group *Cc*, which does not have a 2-fold axis, could not solve the problem. Hence, *C*2/*c* with disordered CH_3 and NH_2 appeared to be the best choice. Further details of the crystallographic information are provided in the Supporting Information. Crystal data and structure refinement parameters for **2**, **3**, and **4** are given in Table 3.

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Supporting Information Available: X-ray structural data for complexes **2**, **3**, and **4**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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