Nitrogen-Linked Diphosphine Ligands with Ethers Attached to Nitrogen for Chromium-Catalyzed Ethylene Tri- and Tetramerizations

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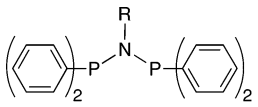
Received February 18, 2006

A series of bis(diphenylphosphino)amine ligands with a donor group attached to the nitrogen linker have been prepared. Metalation of these ligands with chromium trichloride provides precursors to highly active, relatively stable, and selective catalysts for trimerization and tetramerization of ethylene. It has been demonstrated in oligomerization reactions performed at 1 and 4 atm of ethylene that these new systems increase total productivity by enhancing catalyst stability, as compared with those lacking a donor group on the diphosphine ligand. Furthermore, the use of chlorobenzene solvent (rather than toluene) significantly improves productivity, stability, and selectitvity. The product distributions and minor byproducts provide information relevant to mechanistic issues surrounding these types of reactions.

Introduction

In recent years, extensive effort has been made to develop systems that achieve selective oligomerization of linear α-olefins. In particular, 1-hexene and 1-octene stimulate great interest due to their application as comonomers for the production of linear low-density polyethylene. Several ethylene trimerization catalyst systems have been developed,[1] most of which are based on chromium catalysts.[2] Following a report by Wass et al. of a bis(*ortho*-methoxyphenyl)methylaminechromium(III) chloride methylaluminoxane catalyst system that is highly active for ethylene trimerization,[2d] we provided support for their proposed requirement for *ortho*-methoxy functionalities by demonstrating these may act as pendant donors, e.g., as in the structure of $Cr(C_6H_5)_3[P,P,O\text{-}\kappa^3\text{-}(o\text{-}MeO-C_6H_4)_2PN(Me)P(o\text{-}MeO-C_6H_4)_2]$.[2e] More recently, Bollmann and co-workers reported the first chromium catalyst systems to selectively produce 1-octene,[3] using nitrogen-linked diphosphine ligands *not* bearing potentially coordinating ether substituents, e.g., $R_2PN(R')PR_2$ (R = phenyl, naphthyl, ethyl; R′ = alkyl, phenyl). A pendant ether functional group on an aryl substituent is thus not essential for oligomerization activity.[4] We considered the possibility that a PNP ligand having an ether group tethered to the backbone N would have the potential to be a hemilabile tridentate ligand and may therefore provide stability to reactive intermediates or modify the transition states in the oligomerization catalysis.

Herein we report the preparation of some related nitrogen-linked diphosphine ligands (**1**−**4**) bearing an ether donor attached to the amine backbone. Metalation affords the corresponding dimeric chromium(III) chloride complexes as stable precatalysts for the selective trimerization and tetramerization of ethylene. We also report some significant differences between toluene and chlorobenzene as solvent, as well as some mechanistic implications concerning the last steps of the proposed catalytic cycle, inferred from the presence of small amounts of C_6 byproducts in the 1-hexene/1-octene product mixtures.



1: R = $(CH_2)_2OCH_3$
2: R = $(CH_2)_3OCH_3$
3: R = $(o\text{-}OCH_3)C_6H_4$
4: R = $CH_2(o\text{-}OCH_3)C_6H_4$

Results and Discussion

Reactions of ligands **1**−**4** with $CrCl_3(THF)_3$ in methylene chloride (Scheme 1) afford bright bluish-purple chloro-bridged dimers, $[CrCl_2[P,P\text{-}\kappa^2\text{-}(C_6H_5)_2PN(R)P(C_6H_5)_2](\mu_2\text{-}Cl)]_2$ (**5**−**8**). An X-ray structure determination for complex **5** (Figure 1) reveals an edge-sharing bioctahedral arrangement in the solid state, similar to a complex reported by Bollman and co-workers (with the ether oxygen not coordinated to chromium).[3] The other

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(1) For a review, see: Dixon, J. T.; Green, M. J.; Hess, F. M.; Morgan, D. H. *J. Organomet. Chem.* **2004**, *689*, 3641.

(2) (a) Freeman, J. W.; Buster, J. L.; Knudsen, R. D. U.S. Patent 5,856,257 (Phillips Petroleum Company), January 5, 1999. (b) McGuinness, D. S.; Wasserscheid, P.; Keim, W.; Dixon, J. T.; Grove, J. J. C.; Hu, C.; Englert, U. *Chem. Commun.* **2003**, 334. (c) McGuinness, D. S.; Wasserscheid, P.; Keim, W.; Morgan, D. H.; Dixon, J. T.; Bollmann, A.; Maumela, H.; Hess, F. M.; Englert, U. *J. Am. Chem. Soc.* **2003**, *125*, 5272. (d) Carter, A.; Cohen, S. A.; Cooley, N. A.; Murphy, A.; Scutt, J.; Wass, D. F. *Chem. Commun.* **2002**, 858. (e) Agapie, T.; Schofer, S. J.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2004**, *126*, 1304.

(3) Bollmann, A.; Blann, K.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; McGuinness, D. S.; Morgan, D. H.; Neveling A.; Otto, S.; Overett, M.; Slawin, A. M. Z.; Wasserscheid, P.; Kuhlmann, S. *J. Am. Chem. Soc.* **2004**, *126*, 14712.

(4) Overett et al. further asserted that even a single *o*-methoxyphenyl group on the P changed their PNP-based oligomerization catalyst from predominantly tetramerization to a trimerization system, indicating that the oxygen could act as a hemilabile donor. Overett, M. J.; Blann, K.; Bollmann, A.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; Morgan, D. H.; Neveling, A.; Otto, S. *Chem. Commun.* **2005**, 622.

10.1021/om0601596 CCC: $33.50
Publication on Web 09/30/2006

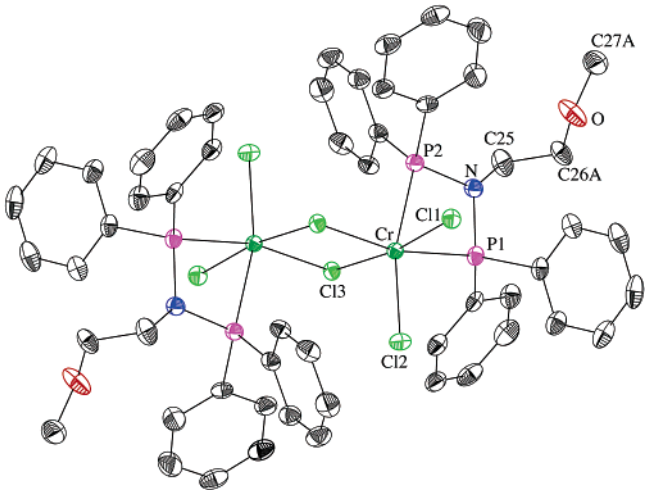
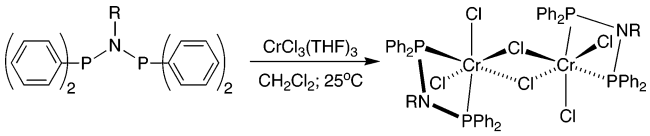


Figure 1. Structural drawing of **5** with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): Cr−P1, 2.4251(6); Cr−P2, 2.4862(6); Cr−Cl1, 2.2701(5); Cr−Cl2, 2.2900(5); Cr−Cl3, 2.3679(5); Cr−Cl3′, 2.3939(5); P1−Cr−P2, 66.837(18); P1−N−P2, 105.01(8); Cl3−Cr−Cl3′, 85.488(17).

Scheme 1



5: R = $(CH_2)_2OCH_3$
6: R = $(CH_2)_3OCH_3$
7: R = $(o\text{-}OCH_3)C_6H_4$
8: R = $CH_2(o\text{-}OCH_3)C_6H_4$

complexes are believed to have analogous $(\mu_2\text{-Cl})_2$-bridged dimeric arrangements.

These new complexes were tested for activity in the trimerization and tetramerization of ethylene. Activation of chlorobenzene solutions of **5**−**8** with methylaluminoxane (MAO) provides active catalysts that give moderate turnover numbers even at 1 atm of ethylene (Table 1). Varying the length and the rigidity of the pendant donor has a significant effect on catalyst activity and stability. The catalyst derived from **8** (Table 1, entries 4−6) is substantially more active than **5** (entry 1), **6** (entry 2), and **7** (entry 3), and its activity reproducibly remains nearly constant for periods of about 2 h, after which time it slowly decreases. Such stability is in contrast with previous work in our group using catalytic systems bearing the ligand $(o\text{-MeO-}C_6H_4)_2PN(Me)P(o\text{-MeO-}C_6H_4)_2$,[2e,5] for which catalyst stability could not reproducibly be maintained over 20 min. In this regard, catalysts derived from **5** and **7** remain stable only 20−30 min before decomposing, as for the ligand system having *ortho*-methoxyphenyl substituents. Total productivity and stability is also lower for catalyst systems employing a bis(diphenylphosphino)amine ligand having no ether group tethered to nitrogen, i.e., **11**: $[CrCl_3(\mathbf{9})]_2$ and **12**: $[CrCl_3(\mathbf{10})]_2$ (**9** = $(C_6H_5)_2PN(CHMe_2)P(C_6H_5)_2$; **10** = $(C_6H_5)_2PN(CH_2(o\text{-Et})C_6H_4)P(C_6H_5)_2$). Presumably, the tether length and rigidity for ligand **4** promotes coordination of the ether group to the active species, increasing its stability. Increased catalyst stability has been demonstrated in experiments run at 1 atm (Figure 2) and 4 atm of ethylene (Figure 3).

The use of chlorobenzene rather than toluene as solvent also appears to result in high activity, stability, and selectivity to 1-hexene and 1-octene, with little polyethylene production (Table 2). Under comparable conditions, reactions employing catalyst **8** in toluene showed much lower productivity and generated higher amounts of polyethylene (Table 2, entry 2). In 1,2-dichlorobenzene catalysts display greater stability than in chlorobenzene, however with slightly lower activity (Table 3, entries 3 and 4). It is not clear whether the beneficial effects of chlorobenzenes are due to weak solvation via the chlorine atom or, more generally, higher solvent polarity. A control reaction was performed in which chlorobenzene and MAO (dried under high vacuum) were allowed to stir in dodecane for several hours at room temperature and up to 60 °C. No reaction products between chlorobenzene and MAO were observed by GC, which confirmed the stability of this solvent under typical oligomerization reaction conditions. Unfortunately, it is not possible to conduct catalytic runs in the noncoordinating polar solvent α,α,α-trifluorotoluene due to the rapid reaction of this solvent with MAO.

Other aspects of the system, such as pressure dependence on activity, selectivity, and product distribution, were further investigated using complex **8** (Table 3). Within the range of pressures tested, the ratio of [1-octene] to [1-hexene] increases linearly with higher concentrations of ethylene (entries 1 to 5), with little or no effect on 1-hexene and 1-octene selectivity within C_6 or C_8 fractions. Higher ethylene pressures are thus expected to further favor 1-octene production, in light of previous reports.[3]

Careful investigations of the product mixture provide valuable insights on the mechanism of tri- and tetramerization of ethylene. It has been previously proposed that the mechanism in the trimerization,[2d,e,6,7] and more recently oligomerization,[8] of ethylene involves chromacyclic intermediates. C_{10} and higher oligomers are presumably formed by incorporation of α-olefins into chromacyclic intermediates.[7] Our results support this assumption, where the main compounds in the C_{10} and C_{12} fractions suggest incorporation of 1-hexene and 1-octene, respectively, into chromacyclics. Furthermore, the relative abundance of these higher oligomers decreases dramatically at short reaction times, where 1-hexene and 1-octene concentrations are relatively low (Table 1, entries 4−6).

Table 1. Ethylene Trimerization/Tetramerization with Complexes 5−8[a]

entry (complex)	time (min)	productivity ($g_{product}/g_{Cr}$)	PE (wt %)	C-6 (wt %)[b]	C-8 (wt %)	C-10 (wt %)[c]	>C-10 (wt %)[d]	1-C6 in C6 (%)	1-C8 in C8 (%)
1 (**5**)	90	361	6	61	31	1	1	83	>90
2 (**6**)	90	403	0.5	62	34	2	2	84	99
3 (**7**)	90	924	0.3	66	27	4	3	91	97
4 (**8**)	90	1625	<0.1	62	24	7	7	93	93
5 (**8**)	270	3106	<0.1	54	23	12	11	93	88
6 (**8**)	1250	6244	0.2	45	16	16	24	92	73

[a] Conditions: $[CrCl_2[P,P\text{-}\kappa^2\text{-}(C_6H_5)_2PN(R)P(C_6H_5)_2](\mu_2\text{-Cl})]_2$ (0.02 mmol), C_6H_5Cl (50 mL), MAO (300 equiv, 10 wt % in toluene), C_2H_4 (1 atm), 25 °C. [b] In the C_6 fraction, hexene isomers appear as 0−0.3 wt %. [c] 1-C_{10} was not detected by GC. [d] C-12 (among which 5-methyl-1-undecene), C-14, C-16, etc.; structures not determined.

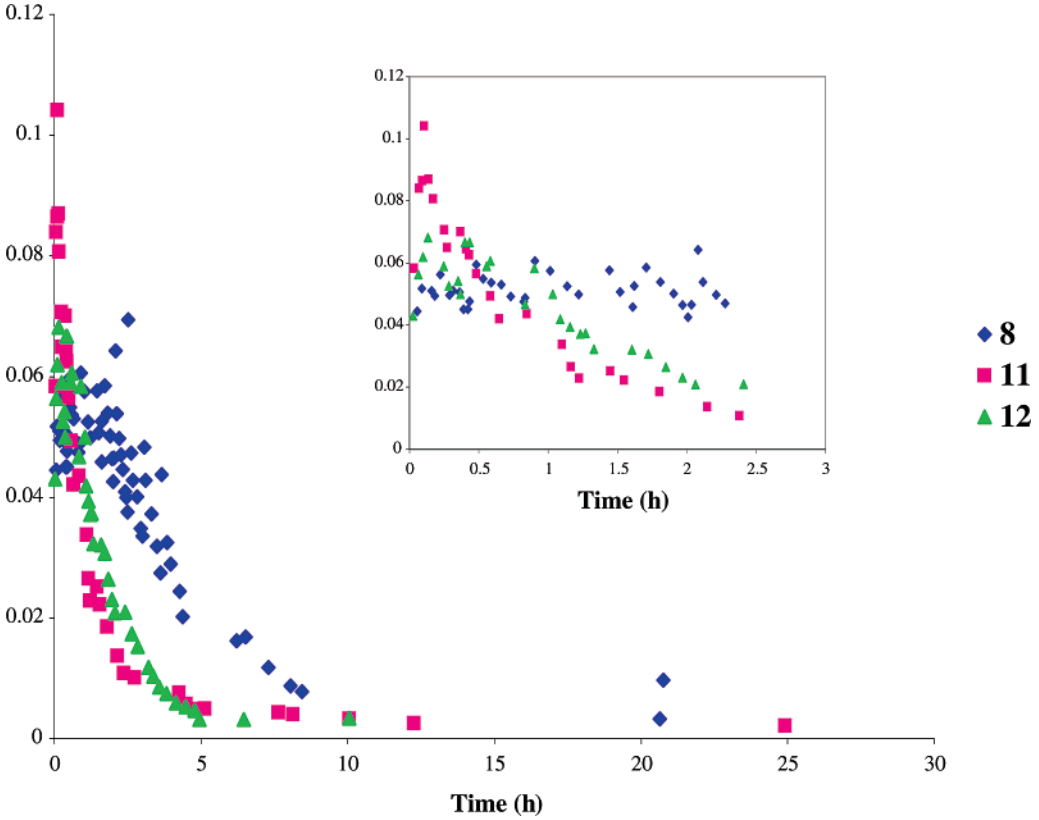
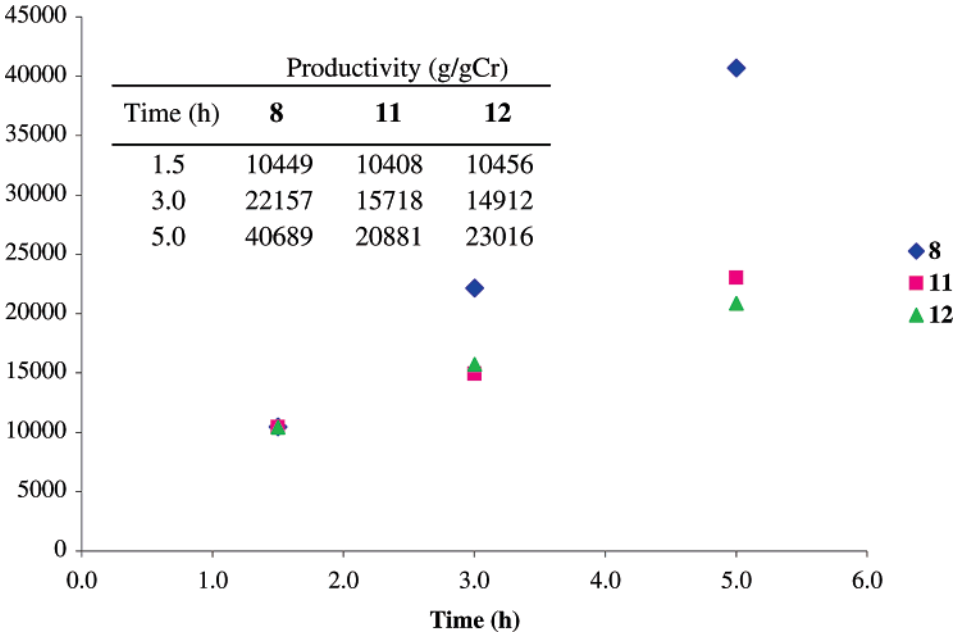


Figure 2. Comparison between catalysts **8**, **11**, and **12**: ethylene consumption over time at 1 atm ethylene.



	Productivity (g/gCr)		
Time (h)	**8**	**11**	**12**
1.5	10449	10408	10456
3.0	22157	15718	14912
5.0	40689	20881	23016

Figure 3. Comparison between catalysts **8**, **11**, and **12**: total productivity over time at 4 atm ethylene.

A series of computational studies on the trimerization reaction with tantalum, titanium, and chromium catalysts have suggested that rather than a stepwise β-H elimination and reductive elimination to liberate 1-hexene, a concerted, metal-assisted 3,7-hydride shift is favored for the metallacycloheptane.[6d−h] A closer look at the C_6 side-products formed in our trimerization/tetramerization reactions revealed that the two main side-products within the C_6 fraction (GC) are methylcyclopentane and methylenecyclopentane. Similar observations have been

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Table 2. Solvent Comparison in the Oligomerization Using Precatalysts 8, 11, and 12

entry (complex)	solvent	*p* (atm)	productivity ($g_{product}/g_{Cr}$)	PE (wt %)	C-6 (wt %)	C-8 (wt %)	C-10 (wt %)	>C-10 (wt %)	1-C6 in C6 (%)	1-C8 in C8 (%)
1 (**8**)[a]	PhCl	4	11 764	0.4	44	33	7	16	90	93
2 (**8**)[a]	toluene	4	822	53	16	29	1	1	72	95
3 (**8**)[b]	1,2-$C_6H_4Cl_2$	1	4011	0.3	46	17	18	19	91	79
4 (**8**)[a]	1,2-$C_6H_4Cl_2$	4	7250	1	39	29	11	20	86	93
5 (**11**)[a]	PhCl	4	7997	4	49	28	8	10	96	92
6 (**11**)[a]	toluene	4	1355	9	34	53	2	2	89	99
7 (**12**)[a]	PhCl	4	10 587	0.2	40	34	8	17	91	93
8 (**12**)[a]	toluene	4	10 66	23	29	46	1	1	84	95

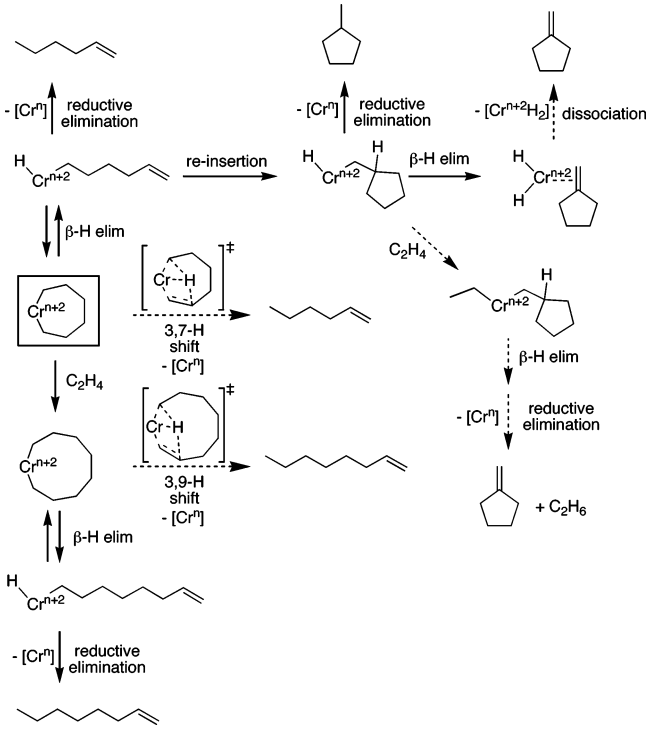
[a] Conditions: $[(PNP)CrCl_3]_2$ (0.02 mmol), solvent (50 mL), MAO (300 equiv, 10 wt % in toluene), 25 °C, 90 min. [b] Conditions: $[(PNP)CrCl_3]_2$ (0.02 mmol), solvent (50 mL), MAO (300 equiv, 10 wt % in toluene), 25 °C, 30 h.

Table 3. Ethylene Trimerization/Tetramerization with Complex 8

entry	*p* (atm)	productivity ($g_{product}/g_{Cr}$)	PE (wt %)	C-6 (wt %)[c]	C-8 (wt %)	C-10 (wt %)	C-12 (wt %)	>C-12 (wt %)	1-C6 in C6 (%)	1-C8 in C8 (%)
1[a]	1	1625	<0.1	62	24	7	5	1	93	93
2[a]	2.4	3911	0.6	57	28	6	6	2	92	94
3[a]	4.1	11 684	0.4	44	33	7	11	5	90	92
4[a]	6.1	14 584	0.2	41	38	6	10	5	87	95
5[b]	8.4	42 408	0.2	30	34	8	17	12	83	93

[a] Conditions: $[(PNP)CrCl_3]_2$ (0.02 mmol), C_6H_5Cl (50 mL), MAO (300 equiv, 10 wt % in toluene), 25 °C, 90 min. [b] Conditions: $[(PNP)CrCl_3]_2$ (0.008 mmol), C_6H_5Cl (20 mL), MAO (300 equiv, 10 wt % in toluene), 90 min. [c] In the C_6 fraction, hexene isomers appear as 0−0.3 wt %.

Scheme 2



recently reported by Overett et al.[7] Both of these products suggest the hexenyl-hydride mediated pathway. Formation of the methylcyclopentane may be readily accommodated by olefin reinsertion into the Cr−C bond followed by C−H reductive elimination (Scheme 2).[9] Methylenecyclopentane could arise from this same cyclopentylmethyl-hydride intermediate, via a second β-H elimination by either pathway shown in Scheme 2. Indeed, it is difficult to envision formation of either of these minor products by any mechanism *not* involving a chromium hydride. Of course, we cannot rule out that, whereas methylcyclopentane and methylenecyclopentane arise from the hexenyl-hydride intermediate, 1-hexene is formed by the principal alternative: a concerted 3,7-hydride shift. Nonetheless, formation of these two minor products does provide some of the only support for the stepwise pathway.

Conclusions

We have shown that chromium(III) complexes of the type $[(PNP)CrCl_3]_2$ containing an ether donor attached directly to the bridging nitrogen form active catalysts for the trimerization and tetramerization of ethylene upon activation with MAO. Furthermore, catalyst activity and lifetime are critically dependent on the ether tether length and rigidity. Chlorobenzene solvents appear to further enhance productivity, stability, and selectivity as compared with toluene. Increasing ethylene pressure favors 1-octene production over that of 1-hexene. Finally, detection of minor C_6 products, methylcyclopentane and methylenecyclopentane, may suggest 1-hexene arises via a stepwise mechanism involving a hexenyl-hydride, rather than a concerted loss by a 3,7-hydride shift from the chromacycloheptane. Further studies of the reaction including mechanistic investigations are in progress.

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. All gases were purified by passage over MnO on vermiculite and activated molecular sieves. Solvents for air- and moisture-sensitive reactions were dried over sodium benzophenone ketyl or calcium hydride or by the method of Grubbs.[1] Chloroform-*d* was purchased from Cambridge Isotopes and dried over activated molecular sieves. Other materials were used as received. *o*-Ethylbenzylamine hydro-

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(9) An alternative pathway could involve 2,1-reinsertion of the olefin into the Cr−H bond to afford a 2-methylchromacyclohexane that subsequently reductively eliminates methylcyclopentane. This possibility appears less likely because the analogous reductive elimination of cyclohexane from the chromacycloheptane (or cyclooctane from the chromacyclononane) is not observed. Moreover, deuterium labeling experiments do not indicate reversible 2,1-reinsertion of the olefin into the Cr−H bond (T. Agapie, J. A. Labinger, and J. E. Bercaw, manuscript in preparation).

chloride was purchased from Rare Chemicals. Other amine starting materials, MAO (10 wt % in toluene), chlorodiphenylphosphine, and $(THF)_3CrCl_3$ were purchased from Aldrich.

Instrumentation. ^1H and ^{31}P NMR spectra were recorded on a Varian Mercury 300 spectrometer at 299.868 and 121.389 MHz, respectively, at room temperature. All ^1H NMR chemical shifts are reported relative to TMS, and ^1H (residual) chemical shifts of the solvent are used as secondary standard. ^{31}P NMR chemical shifts are reported relative to an external H_3PO_4 standard. GC measurements were taken on an Agilent 6890 Series GC using an Agilent HP-5 column. X-ray crystallography was carried out by Dr. Michael W. Day and Lawrence M. Henling using an Enraf-Nonius CAD-4 diffractometer.

Synthesis of $(C_6H_5)_2PN(CH_2CH_2OCH_3)P(C_6H_5)_2$ (1). Chlorodiphenylphosphine (4.5 mL, 24 mmol, 2.3 equiv) was dissolved in dry toluene (150 mL). Under an atmosphere of argon, an excess of triethylamine (5.0 mL, 36 mmol) was syringed into the reaction flask, which was stirred for 5 min. 2-Methoxyethylamine (0.9 mL, 10 mmol) was then syringed dropwise under argon. A precipitate immediately formed. The reaction mixture was then allowed to stir for 36 h at 110 °C. The ammonium salt was filtered off, and the solvent and the excess triethylamine and diphenylphosphine were removed in vacuo to leave a yellow residue. The residue was passed through a silica gel plug using a CH_2Cl_2 (15%)/petroleum ether (85%) mixture as the eluent. Removing the solvent afforded 2.905 g of a fine white powder in 63% yield. ^1H NMR (RT, 300 MHz, $CDCl_3$): δ 2.90 (2H, t, $J_{HH} = 7.4$ Hz, CH_2O), 3.02 (3H, s, OCH_3), 3.47 (2H, m, CH_2), 7.29−7.44 (20H, m, Ar*H*). ^{31}P NMR (RT, 121 MHz, $CDCl_3$): δ 64.6 ppm (s). MS (FAB+): 444 (M + H).

Synthesis of $(C_6H_5)_2PN(CH_2CH_2CH_2OCH_3)P(C_6H_5)_2$ (2). Chlorodiphenylphosphine (4.9 mL, 26 mmol, 2.5 equiv) was dissolved in dry toluene (150 mL). Under an atmosphere of argon, an excess of triethylamine (8.0 mL, 58 mmol) was syringed into the reaction flask, which was stirred for 5 min. 3-Methoxypropylamine (1.1 mL, 11 mmol) was then syringed dropwise under argon. A precipitate immediately formed. The reaction mixture was then allowed to stir for 36 h at 110 °C. The ammonium salt was filtered off, and the solvent and the excess triethylamine and diphenylphosphine were removed in vacuo to leave a yellowish residue. The residue was passed through a silica gel plug using a CH_2Cl_2/petroleum ether (1:1) mixture as the eluent. Removing the solvent and trituration with petroleum ether afforded 3.564 g of a fine white powder in 75% yield. ^1H NMR (RT, 300 MHz, $CDCl_3$): δ 1.39 (2H, br tt, $J_{HH} = 8.1$ Hz, $J_{HH} = 6.3$ Hz, CH_2), 3.03 (2H, t, $J_{HH} = 6.3$ Hz, CH_2O), 3.10 (3H, s, OCH_3), 3.27−3.44 (2H, m, NCH_2), 7.28−7.46 (20H, m, Ar*H*). ^{31}P NMR (RT, 121 MHz, $CDCl_3$): δ 63.1 ppm (s). MS (FAB+): 458 (M + H).

Synthesis of $(C_6H_5)_2PN((o\text{-}OCH_3)C_6H_4)P(C_6H_5)_2$ (3). Chlorodiphenylphosphine (5.8 mL, 31 mmol, 2.3 equiv) was dissolved in dry THF (150 mL). Under an atmosphere of argon, an excess of triethylamine (9.0 mL, 65 mmol) was syringed into the reaction flask, which was stirred for 5 min. *o*-Anisidine (1.5 mL, 14 mmol) was then syringed dropwise under argon. A precipitate immediately formed, and the mixture turned deep yellow. The reaction mixture was then allowed to stir for 24 h at 62 °C. The reaction can only afford about 75% conversion (longer reaction times do not increase conversion). The solvent and the excess trimethylamine and diphenylphosphine were removed in vacuo. The yellow residue was dissolved in CH_2Cl_2 and washed with 10% NaOH. The organic fraction was dried over $MgSO_4$ and the solvent removed after filtration, which afforded a yellow oil. After dissolving the oil in a minimum amount of CH_2Cl_2, petroleum ether was added and a white powder crashed out at room temperature to give 4.642 g of the desired compound in 70% yield. ^1H NMR (RT, 300 MHz, $CDCl_3$): δ 3.29 (3H, s, OCH_3), 6.79−6.71 (1H, m, Ar*H*), 7.01−7.11 (1H, m, Ar*H*), 7.16−7.51 (20H, m, Ar*H*), 7.55−7.65 (1H, m, Ar*H*), 7.73−7.83 (1H, m, Ar*H*). ^{31}P NMR (RT, 121 MHz, $CDCl_3$): δ 65.5 ppm (s). MS (FAB+): 491 (M + H).

Synthesis of $(C_6H_5)_2PN(CH_2(o\text{-}OCH_3)C_6H_4)P(C_6H_5)_2$ (4). Chlorodiphenylphosphine (4.6 mL, 24.7 mmol, 2.5 equiv) was dissolved in dry CH_2Cl_2 (150 mL). Under an atmosphere of argon, an excess of triethylamine (7.0 mL, 50.6 mmol) was syringed into the reaction flask, which was stirred for 5 min. 2-Methoxybenzylamine (1.3 mL, 9.9 mmol) was then syringed dropwise under argon. A precipitate immediately formed, and the mixture turned deep yellow. The reaction mixture was then allowed to stir for 14 h at 37 °C. The solvent and the excess trimethylamine and diphenylphosphine were removed in vacuo. The yellow residue was dissolved in CH_2Cl_2 and washed with 10% NaOH. The organic fraction was dried over $MgSO_4$ and the solvent removed after filtration, which afforded an off-white solid. After dissolving the solid in a minimum amount of CH_2Cl_2, acetonitrile was added and a white powder crashed out at room temperature to give 3.366 g of the desired compound in 67% yield. ^1H NMR (RT, 300 MHz, $CDCl_3$): δ 3.70 (3H, s, OCH_3), 4.47 (2H, t, $J_{HP} = 9.2$ Hz, CH_2), 6.66−6.84 (3H, m, NCH_2Ar*H*), 7.09−7.18 (1H, m, NCH_2Ar*H*), 7.22−7.32 (12H, m, Ar*H*), 7.35−7.44 (8H, m, Ar*H*). ^{31}P NMR (RT, 121 MHz, $CDCl_3$): δ 59.94 ppm (s). MS (direct insertion probe EI): 505.17.

Synthesis of $(C_6H_5)_2PN(CHMe_2)P(C_6H_5)_2$ (9). Chlorodiphenylphosphine (4.0 mL, 21.5 mmol, 2.3 equiv) was dissolved in dry CH_2Cl_2 (150 mL). Under an atmosphere of argon, an excess of triethylamine (5.5 mL, 39.8 mmol) was syringed into the reaction flask, which was stirred for 5 min. Isopropylamine (0.8 mL, 9.4 mmol) was then syringed dropwise under argon. The reaction mixture was then allowed to stir for 14 h at room temperature. The solvent and the excess trimethylamine and diphenylphosphine were removed in vacuo. The yellow residue was dissolved in Et_2O and washed with 1 M NaOH. The organic fraction was dried over $MgSO_4$ and the solvent removed after filtration, which afforded an off-white oil. After dissolving the oil in a minimum amount of CH_2Cl_2, acetonitrile was added and a white powder crashed out at room temperature to give 2.823 g of the desired compound in 71% yield. ^1H NMR (RT, 300 MHz, $CDCl_3$): δ 1.15 (6H, d, $J_{HH} = 6.5$ Hz, CH(CH_3)$_2$), 3.76 (1H, m, C*H*Me$_2$), 7.25−7.41 (20H, m, Ar*H*). ^{31}P NMR (RT, 121 MHz, $CDCl_3$): δ 49.5 ppm (s).

Synthesis of $(C_6H_5)_2PN(CH_2(o\text{-}Et)C_6H_4)P(C_6H_5)_2$ (10). Chlorodiphenylphosphine (1.9 mL, 10.1 mmol, 2.3 equiv) was dissolved in dry CH_2Cl_2 (80 mL). Under an atmosphere of argon, an excess of triethylamine (3.5 mL, 25.3 mmol) was syringed into the reaction flask, which was stirred for 5 min. *o*-Ethylbenzylamine hydrochloride (0.750 g, 4.4 mmol), as a CH_2Cl_2 suspension, was then added to the reaction flask. The reaction mixture was then allowed to stir for 14 h at room temperature. The solvent and the excess trimethylamine and diphenylphosphine were removed in vacuo. The yellow residue was dissolved in CH_2Cl_2 and washed with 10% NaOH. The organic fraction was dried over $MgSO_4$ and the solvent removed after filtration, which afforded an off-white oil. After dissolving the oil in a minimum amount of CH_2Cl_2, acetonitrile was added and a white powder crashed out at room temperature to give 1.474 g of the desired compound in 67% yield. ^1H NMR (RT, 300 MHz, $CDCl_3$): δ 1.11 (3H, t, $J_{HH} = 7.6$ Hz, CH_2CH_3), 2.59 (2H, q, $J_{HH} = 7.6$ Hz, CH_2CH$_3$), 4.46 (2H, t, $J_{HP} = 9.7$ Hz, NCH_2-Ar), 6.66−6.75 (1H, m, NCH_2Ar*H*), 6.87−6.97 (1H, m, NCH_2-Ar*H*), 7.05−7.12 (2H, m, NCH_2Ar*H*), 7.19−7.45 (20H, m, Ar*H*). ^{31}P NMR (RT, 121 MHz, $CDCl_3$): δ 59.8 ppm (s). MS (direct insertion probe EI): 503.19.

Synthesis of Complexes 5−8. In the glovebox, compound **1**, **2**, **3**, or **4** was dissolved in CH_2Cl_2 (3 mL). $(THF)_3CrCl_3$ (1 equiv) was dissolved in CH_2Cl_2 (7 mL) in a separate vial. The chromium starting material solution was slowly added to the stirring solution of the ligand. The mixture, which immediately turned blue, was allowed to react for 10 min, after which the solvent was pumped off. The residue was triturated twice with CH_2Cl_2. The remaining

solid was recrystallized from CH_2Cl_2/petroleum ether to give a bright blue-violet powder (**5**: 76% yield; **6**: 90% yield; **7**: 25% yield; **8**: 86% yield).

Synthesis of Complexes 11 and 12. In the glovebox, compound **9** or **10** was dissolved in CH_2Cl_2 (3 mL). $(THF)_3CrCl_3$ (1 equiv) was dissolved in CH_2Cl_2 (7 mL) in a separate vial. The chromium starting material solution was slowly added to the stirring solution of the ligand. The mixture, which immediately turned blue, was allowed to react for 10 min, after which the solvent was pumped off. The residue was triturated twice with CH_2Cl_2. The remaining solid was recrystallized from CH_2Cl_2/petroleum ether to give a bright blue-violet powder (**11**: 84% yield; **12**: 73% yield).

General Procedure for Oligomerization of C_2H_4 (1 atm) with 5−8/MAO. In the glovebox, a 250 mL round-bottom flask was charged with **5**, **6**, **7**, or **8** (0.020 mmol, 1 equiv) in 50 mL of PhCl to give a pale bluish-purple solution. The flask was equipped with a 180° needle valve, fully degassed on the vacuum line at −78 °C. The system was allowed to warm to 20 °C and was backfilled with 1 atm of ethylene. With a positive pressure of ethylene, the valve was replaced with a septum and MAO (10 wt % in toluene, 3.2 mL, 300 equiv) was syringed in. The mixture immediately turned green upon addition. Ethylene consumption was monitored using a mercury manometer. After the indicated reaction time, the mixture was quenched with HCl/MeOH. An aliquot of the organic fraction was separated and filtered through a plug of activated alumina to remove any chromium. This mixture was analyzed by GC and GC-MS. All identified products were quantified by comparison to a mesitylene standard, which was added to the reaction mixture. The reaction mixture was then filtered, and any solid was washed with HCl/MeOH and dried under vacuum for 15 h and weighed.

General Procedure for Oligomerization of C_2H_4 at High Pressure (Table 2, entries 1−4). In the glovebox, a 225 mL high-pressure glass vessel was charged with **8** (0.020 mmol, 1 equiv) in 50 mL of PhCl to give a pale bluish-purple solution. The vessel was equipped with a regulator and placed on the high pressure setup. Ethylene was purged through the system, after which MAO (10 wt % in toluene, 3.2 mL, 300 equiv) was added via syringe. The mixture immediately turned green upon addition. Ethylene pressure was kept constant during the reaction (90 min), after which the system was vented and the reaction mixture quenched with HCl/MeOH. An aliquot of the organic fraction was separated and filtered through a plug of activated alumina to remove any chromium. This mixture was analyzed by GC and GC-MS. All identified products were quantified by comparison to a mesitylene standard, which was added to the reaction mixture. The reaction mixture was then filtered, and any solid was washed with HCl/MeOH and dried under vacuum for 15 h and weighed.

General Procedure for Oligomerization of C_2H_4 at High Pressure (Table 2, entry 5). The procedure is the same as above; however a 85 mL high-pressure glass vessel was employed for the reaction. Furthermore, 0.008 mmol of **8**, 20 mL of PhCl, and 1.3 mL of MAO solution in toluene (300 equiv) were used.

Acknowledgment. We thank Dr. Steven A. Cohen (Innovene, now Ineos) for helpful discussions and Michael W. Day and Lawrence M. Henling (Caltech) for assistance with single-crystal X-ray crystallographic studies. We are grateful to BP Chemicals and Innovene for financial support.

Supporting Information Available: X-ray determination, tables of bond lengths, angles, and anisotropic displacement parameters for the structure of **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0601596