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Selective Ethylene Tri-/Tetramerization Catalysts

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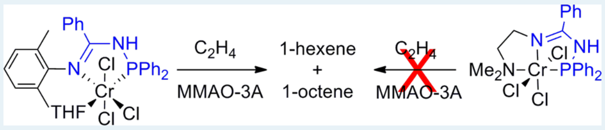
S *Supporting Information*



ABSTRACT: A new family of highly active ethylene tri-/tetramerization catalysts based on *N*-phosphinoamidinechromium complexes has been investigated. The 1-hexene to 1-octene molar ratio can be tuned from 140 to 1.5 by varying the steric environment around the chromium center, and product purities are very good to excellent. Precatalyst tridentate coordination effectively shuts down catalytic activity, suggesting that THF abstraction from the chromium center by the Lewis acidic aluminum activator is necessary to achieve an active catalyst system.

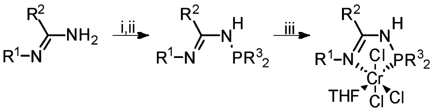
KEYWORDS: *ethylene oligomerization, chromium, P,N-ligands, hexene, octene*

Linear α-olefins (LAOs) are primarily manufactured as a broad distribution (Schulz−Flory or Poisson) by metal-catalyzed ethylene oligomerization (M = Ni, Shell; Al, Chevron Phillips, Ineos).[1] The overweighted demand growth and profitability of the light fraction LAOs 1-hexene and 1-octene versus the heavier fractions (and 1-butene) has stimulated significant academic and industrial research into selective ethylene tri-/tetramerization catalysts.[2−4] The first commercial implementation of this "dial a fraction" concept was Chevron Phillips's selective 1-hexene catalyst technology.[5]

A catalyst system (Cr/PNP) first described by BP researchers and later found by Sasol researchers to be capable of selective ethylene tri-/tetramerization has been thoroughly investigated;[6−8] however, despite extensive ligand modification, achieving high 1-hexene purity without compromising catalyst performance has remained a challenge.[9,10] Ideally, comonomer-grade LAOs contain >99 wt % α-olefin; low α-content requires distillation, causing yield loss and higher process costs. Similar challenges have been reported in other bisphosphine-based ethylene tri-/tetramerization catalyst systems.[2−4,11−14] Moreover, reports of selective ethylene tri-/tetramerization catalysts using bidentate ligand frameworks other than P,P-based systems are lacking.[15,16] P,N-ligands[17−21] provide more steric and electronic flexibility than their P,P or N,N equivalents, and this has been demonstrated in extensive studies on nickel-catalyzed ethylene oligomerization.[22] Therefore, we have chosen to focus our efforts on developing a P,N-ligand synthesis that would provide facile access to catalysts with varied steric environments. Although electronically, asymmetric ligands can present challenges in catalytic chemistry and often do not perform as well as their homoditopic parent compounds,[23] herein, we present a modular P,N-ligand system, *N*-phosphinoamidine, and its use in producing a new class of high-activity, selective 1-hexene/1-octene catalysts.[24] We will show that adding a third donor to the P,N-ligand backbone, producing a tridentate ligand, renders the resulting Cr(III) complex essentially inactive for ethylene tri-/tetramerization.

The target *N*-phosphinoamidine ligands **2a−f** were generated in high yield (typically 90+ wt %) by salt metathesis of the in situ-generated lithium amidinates and the corresponding chlorophosphines (Scheme 1). The precursor amidines **1a−f** (note **1b** = **1c** = **1d**) were conveniently synthesized starting from the respective nitrile and aniline using a previously reported procedure.[25] Each amidine precursor was characterized by ^{1}H and ^{13}C NMR spectroscopy, and the data were consistent with a single amidine isomer. *N*-phosphino amidines afforded more complicated ^{1}H NMR spectra, which have been interpreted as an equilibrium mixture of two tautomers that interconvert slowly (on the NMR time scale) at room temperature. The tautomers for **2a** are shown as **A** (major) and **B** (minor) in Scheme 2.

Scheme 1[a]



1a	2a	3a (R^1=2,6-Me$_2$C$_6$H$_3$, R^2=Ph, R^3=Ph)
1b	2b	3b (R^1=2,6-Me$_2$C$_6$H$_3$, R^2=4-*t*BuC$_6$H$_4$, R^3=iPr)
1c	2c	3c (R^1=2,6-Me$_2$C$_6$H$_3$, R^2=4-*t*BuC$_6$H$_4$, R^3=Ph)
1d	2d	3d (R^1=2,6-Me$_2$C$_6$H$_3$, R^2=4-*t*BuC$_6$H$_4$, R^3=Et)
1e	2e	3e (R^1=2,6-Me$_2$C$_6$H$_3$, R^2=4-MeBz, R^3=Ph)
1f	2f	3f (R^1=3,5-Me$_2$C$_6$H$_3$, R^2=Ph, R^3=*i*Pr)

[a]Reagents and conditions: (i) ^{n}BuLi, Et$_2$O, 0 °C; (ii) R$^3_2$PCl, Et$_2$O, 25 °C; (iii) CrCl$_3$(THF)$_3$, THF, 25 °C.

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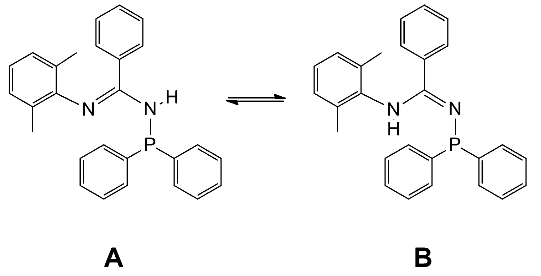
Scheme 2. Proposed Tautomers for *N*-Phosphinoamidine Ligand 2a



^{1}H NMR evidence supporting the presence of tautomers includes the observance of two resonances in the N−H region, one a doublet (δ 5.39, $^2J_{PH}$ = 6.9 Hz) consistent with structure **A**, and the other a broad singlet (δ 4.94) consistent with structure **B**. In addition, each N−H resonance has associated methylaryl resonances with the corresponding integrated intensities. Variable temperature NMR studies on **2a** (65:35 mixture of **A** to **B** at 25 °C) show that the two N−H and methylaryl resonances each begin to coalesce into single broad resonances at 60 °C. Similar behavior was observed for **2b** at 60 °C (85:15 mixture of tautomers at 25 °C). It is difficult to rationalize the observed N−H resonances if the *N*-phosphino amidines are simply a mixture of *E* (major) and *Z* (minor) isomers of a single tautomer. Furthermore, each *N*-phosphino amidine was characterized by electron impact mass spectroscopy (EI-MS). A molecular ion peak $[M]^+$ was observed for all P,N-ligands, confirming the constitutional integrity of these ligands. It should be noted that *N*,*N*-bisphosphino amidines were not observed by mass spectrometry, despite the presence of a reactive amidine hydrogen.

Treatment of $CrCl_3(THF)_3$ with **2a**−**f** in THF, followed by solvent removal and washing with pentane, produced blue to blue-green solids (**3a**−**f**). Complex **3a** was dissolved in acetonitrile and layered with diethylether to produce X-ray quality single crystals. X-ray analysis of **3a·MeCN** verified κ^2-P,N chelation to the octahedrally coordinated chromium center (Figure 1). The structure is consistent with localized bonding within the ligand (N2−C13, 1.300(3) Å; N1−C13, 1.356(3) Å) and with selective binding of the major tautomer of **2a**.[26−28] The acetonitrile molecule binds trans to the strong field phosphorus atom to complete the octahedral coordination environment. A second acetonitrile is present in the crystal lattice and is hydrogen-bonded to the amidine NH group. Elemental analyses of complexes **3a**−**f** synthesized and recrystallized from THF are consistent with THF occupying chromium's sixth coordination site. Room temperature magnetic moments (μ_{eff} = 3.7−3.9 μ_B) indicate that **3a**−**f** contain *S* = 3/2 spin centers.

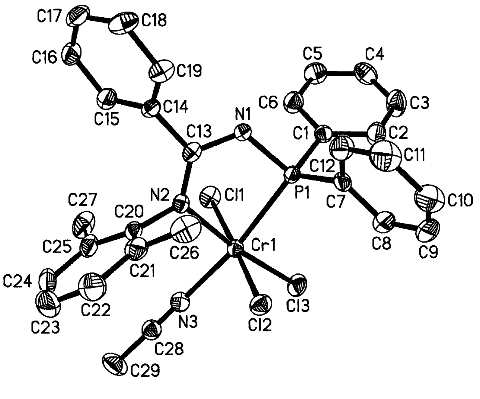


Figure 1. Molecular structure of **3a·MeCN** with atoms at the 50% probability level. Selected bond distances (Å): Cr1−P1, 2.4225(7); Cr1−N2, 2.1286(16); Cr1−N3, 2.0682(19); N2−C13, 1.300(3); N1−C13, 1.356(3); N1−P1, 1.7014(17).

The precatalysts **3a**−**f**, when activated with MMAO (400−800 equiv) in the presence of ethylene and hydrogen,[29] produce very active, selective 1-hexene/1-octene catalysts (Table 1). Mixed decenes and dodecenes, generated from the cotrimerization of 1-hexene or 1-octene with ethylene, were also formed in small amounts along with polyethylene.[8] The 1-hexene/1-octene ratio is clearly dependent on the catalyst structure. Smaller phosphino groups ($-PR^3_2$) produce more 1-octene under comparable conditions: **3b** (R^3 = ^{i}Pr, 0.9 wt %); **3c** (R^3 = Ph, 12.0 wt %); **3d** (R^3 = Et, 15.0 wt %). Precatalyst **3e**, which contains the most sterically open ligand framework, produced the highest amount of 1-octene (70 °C, 30.5 wt %; 50 °C, 44.7 wt %). The 1-hexene purity (wt % 1-hexene in the C6 fraction) decreased upon reducing the reaction temperature (70 °C, 97.3 wt %; 50 °C, 94.6 wt %) at 60 bar ethylene, although the 1-octene purity did not change significantly. Since ethylene solubility increases at lower temperatures under isobaric conditions,[30] the ethylene pressure was adjusted to equate the solution ethylene concentrations at different temperatures. Even with this adjustment it was again observed that more 1-octene was produced at lower temperatures (70 °C, 60 bar, 30.5 wt % C_8; 50 °C, 48 bar, 41.9 wt % C_8). It should be noted that higher solution concentrations of ethylene produced slightly higher amounts of 1-octene (48 bar, 41.9 wt %; 60 bar, 44.7 wt %) at 50 °C while simultaneously decreasing 1-hexene production. This result, although not definitive, is consistent with a higher reaction order in ethylene concentration for 1-octene versus 1-hexene formation under these reaction conditions.[31] Introducing ligand bulk by substitution at the 2- and 6-aryl positions on the imino group was critical to maintaining high product purity (**3a**−**e**). Complex **3f**, on the other hand, with the methyl groups at the 3- and 5-positions produces very low purity 1-hexene (44.6 wt %) and 1-octene (84.0 wt %) at 70 °C. Major C6 impurities include the cyclization products methylcyclopentane (25.4 wt %) and methylene cyclopentane (27.3 wt %) as well as the hydrogenation product *n*-hexane (2.6 wt %). The increased C_8 production for **3f** (33.7 wt %) versus **3b** (0.9 wt %) is

Table 1. Selected Ethylene Oligomerization Data[a]

precat	*T* (°C)	yield (g)	activity (kg/mol·h)	C_6[b] [1-C_6] (% mass)	C_8[b] [1-C_8] (% mass)	polymer[b] (% mass)
3b	70	284.0	54 700	93.6 [>99]	0.9 [98]	trace
3c	70	17.3	3 690	85.4 [99]	12.0 [98]	2
3d	70	61.7	13 030	79.3 [99]	15.0 [>99]	trace
3e	70	118.1	23 410	65.2 [97]	30.5 [>99]	2
3e	50	92.4	18 460	51.7 [95]	44.7 [99]	>1
3e[c]	50	92.1	17 230	54.8 [95]	41.9 [99]	<1
3f	70	190.9	35 170	52.2 [45]	33.7 [84]	4
4	55	1.2	0	trace	trace	100

[a] Standard 1 L batch reactor conditions: 0.009−0.010 mmol of Cr precatalyst, 400−800 equiv of MMAO-3A, 400 mL of cyclohexane, 2 bar H_2, 60 bar C_2H_4 fed on-demand, 30 min. [b] Mass % of liquid + solid products. [c] 48 bar C_2H_4.

consistent with a less sterically encumbered active site, and catalyst productivity remained robust.

It was surprising to us that precatalyst **3b** forms such a highly active ethylene trimerization catalyst (54 670 kg (C_6 + C_8)/mol·h, 70 °C, TOF = 560 s^{-1}), since to the best of our knowledge, most high-activity ethylene *trimerization* precatalysts contain tridentate ligand systems that coordinate in a *meridonal* or *facial* fashion, whereas most ethylene *tetramerization* precatalysts are coordinated by bidentate ligands.[2−4,32,33] The structure of the catalytic active site is a matter of great interest and open debate. It is possible that the coordinated THF in **3b** remains bound to the chromium center after activation, thereby maintaining tris ligation. Another possibility is that the acidic NH or unsaturated C═N group in **3b** could react with alkylaluminum species present in MMAO, thereby modifying the chromium coordination sphere.[34]

Chromium complex **4**, containing a pendant donor, was synthesized to investigate the effect of adding a third ligand donor group to the *N*- phosphino amidine backbone.[35] X-ray analysis of **4** showed that *mer-κ*^{3}-N,N,P ligand coordination was achieved (Figure 2). As observed for **3a**, the ligand maintains localized bonding (N2−C5, 1.290(4) Å; N3−C5, 1.360(4) Å). Compared with **3a**, the Cr−N2 distance in **4** is ~0.1 Å shorter, presumably because of the enforced tridentate ligand structure. Surprisingly, and in contrast to other Cr(III) precatalysts supported by tridentate ligands,[36,37] **4** does not oligomerize ethylene when activated with MMAO-3A and produced only trace amounts of polyethylene (Table 1). Although not definitive, this result suggests that THF abstraction from **3a**−**f** by the Lewis acidic aluminum activator is necessary to achieve an active catalyst supported by the P,N ligand system.

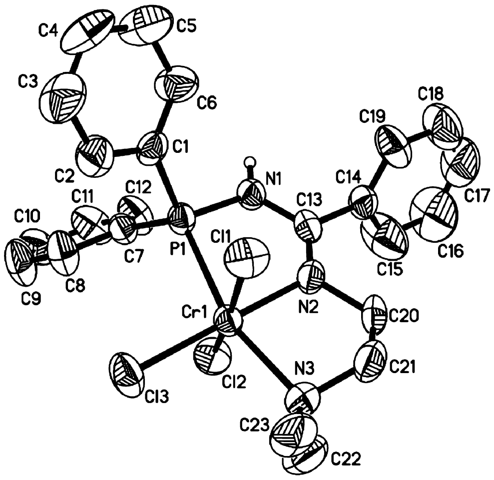


Figure 2. Molecular structure of **4** with atoms at the 50% probability level (hydrogen atoms omitted for clarity). Selected bond distances (Å): Cr1−P1, 2.4360(10); Cr1−N2, 2.030(3); Cr1−N3, 2.162(9); N2−C13, 1.290(4); N1−C13, 1.360(4); N1−P1, 1.704(3).

In summary, we report a new family of selective 1-hexene/1-octene catalysts based on *N*-phosphino amidine ligands. These highly modular ligands are readily synthesized in high yields from simple, widely available precursors. The 1-hexene-to-1-octene ratio can be tuned by varying the steric properties of the ligand, and both 1-hexene and 1-octene product purities are very good to excellent. It has also been shown that tridentate coordination effectively shuts down catalyst activity.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete experimental details, representative NMR spectra, and crystallographic data (CIF) for **3a** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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