APPENDIX A

Homobimetallic Chromium Complexes for Olefin Oligomerization and Polymerization

Abstract

Towards improved selective oligomerization technologies for the preparation of α-olefins, the reactivity of mono- and bisphenoxyiminoquinolines in the presence of chromium, ethylene, and methylaluminoxane activators was explored. A series of Cr complexes supported by phenoxyiminoquinoline ligands was prepared. In oligomerization/polymerization trials, insoluble polyethylene as well as a distribution of oligomers was observed. Higher activity was observed with the bisphenoxyiminoquinoline scaffold versus the monometallic control. Synthesis of a triptycenyl-substituted phenoxyiminoquinoline, reported in the literature to display higher activity and selectivity for α-olefin in ethylene oligomerization is proposed to aid in optimization of reaction conditions for the newly synthesized compounds. Substitution of aryl linker and of the quinoline ring is proposed for engendering selectivity in the oligomers distribution observed in catalytic trials.

INTRODUCTION

Linear α-olefins (LAOs) are key building blocks in the large-scale synthesis of plastics, detergents, lubricants and related petrochemical products.[1] LAOs are produced industrially the oligomerization of ethylene or by the Fischer-Tropsch[2] process. High costs are incurred in the separation of mixtures of LAOs. Current industrial technology for the production of LAOs include full range, on-purpose, and upgrading strategies, which generate mixtures of LAOs, selectively generate one LAO, or convert a hydrocarbon feed to a desired LAO product, respectively.[3] Production of insoluble higher molecular weight polymers necessitates halting an industrial process to remove the generated polymer and wastes hydrocarbon feedstocks. Distillation can be effective in the separation of olefins of different length but mixtures of internal olefins are difficult to separate from one another.[1] Thus, the development of methods for production of single α-olefins in high purity is an important area of research.

The Shell Higher Olefin Process (SHOP) is used to produce ca. 1,000,000 tons/yr. of α-olefins in a Schulz-Flory distribution using Ni and diarylphosphinoacetic acids.[4] The Phillips trimerization system (Cr, 2,5-dimethyl-pyrrole, and alkylating agent) is used to produce ca. 50,000 tons/yr. of 1-hexene from ethylene.[1b,5] Dimerization of 1,3-butadiene has been employed by Dow Chemical to produce 1-octene selectively.[6] Ethylene tetramerization has also been reported and a commercial process using Cr and PNP donor ligands has been developed by Sasol.[7] Improved and complimentary processes for the selective oligomerization of LAOs from ethylene with little to no polymer production are highly desirable.

Gibson and co-workers have reported phenoxyiminoquinoline Cr compounds produce a near Schulz-Flury distribution of LAOs (the distribution is perturbed

Figure A.1a. Cossee Mechanism for Ethylene Oligomerization/Polmerization.

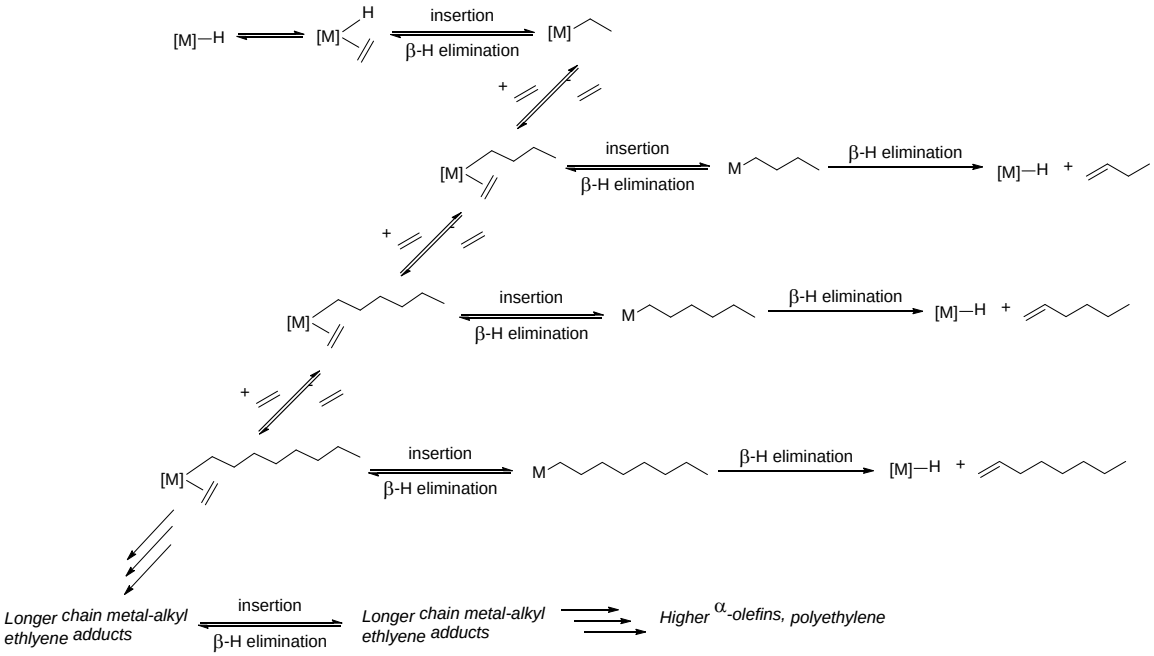
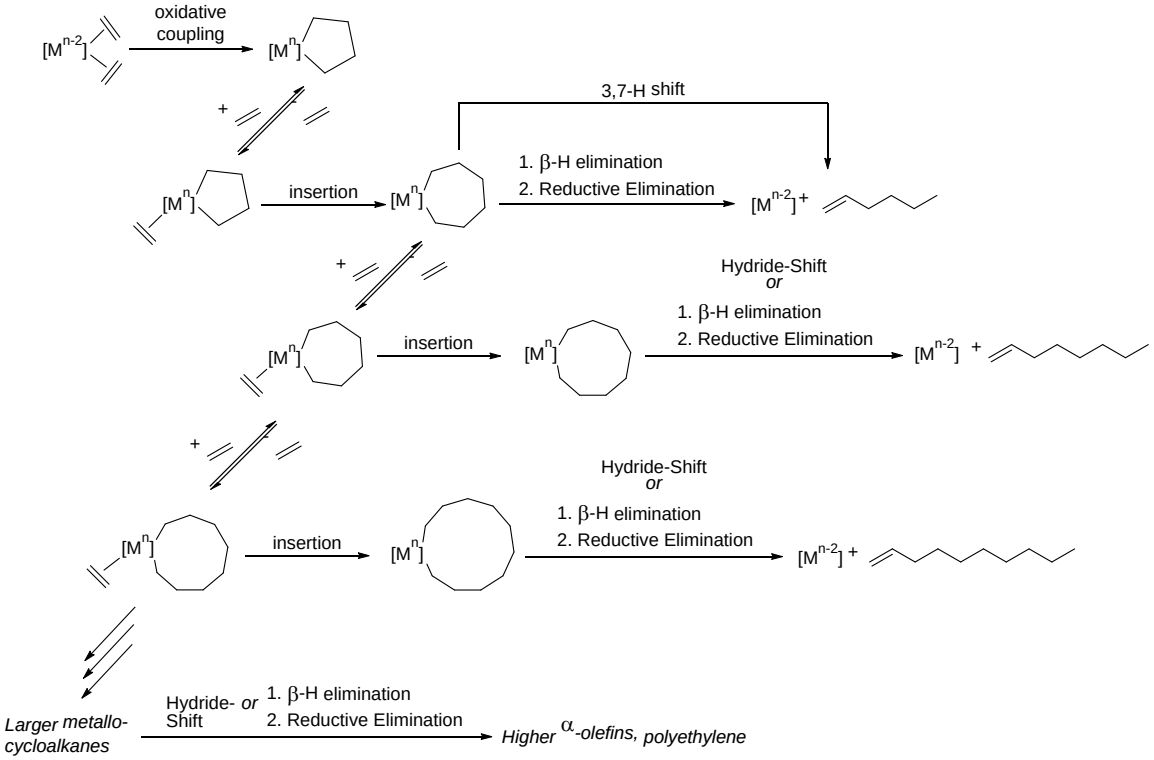
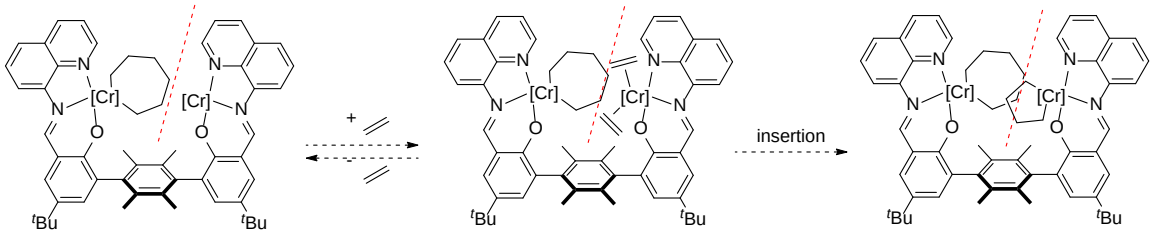


Figure A.1b. Metallocyclic Mechanism for Ethylene Oligomerization/Polmerization.



slightly by chain transfer to Al).[8] Deuterium-labeling experiments performed with a 1:1 C_2H_4:C_2D_4 mixture provided evidence for a metallocyclic versus Cossee mechanism (see Figure A.1a and A.1b).[8c,8d] In a high-throughput screen, oligomerization and/or polymerization activity was demonstrated to vary depending on phenoxyiminoquinoline substitution, with *ortho*-triptycenyl substitution affording a precatalyst (**39,** see Table A.1) with an activity of 7450 g·mmol^{-1}·h^{-1}·bar^{-1} with 98.9% LAO selectivity.[8a,8b] Our group has reported that a bimetallic effect inhibits the deactivation of dinickel bisphenoxyiminato compounds for ethylene polymerization by Lewis bases,[9] facilitates the insertion polymerization of polar monomers by dinickel bisphenoxyiminato without masking of the heteroatom group,[10] and increases the isotacticity of polypropylene and polyhexene generated by dizirconium amine bis(phenolate) versus previously reported monometallic analogues.[11] In a similar strategy, a bimetallic effect was envisioned to possibly encourage elimination of metallocycles of a specific size to result in production selective production of LAOs through ethylene oligomerization.

Figure A.2. Effect of Tethered Cr on Metallocycle Growth in Hypothetical Intermediate in Ethylene Oligomerization.



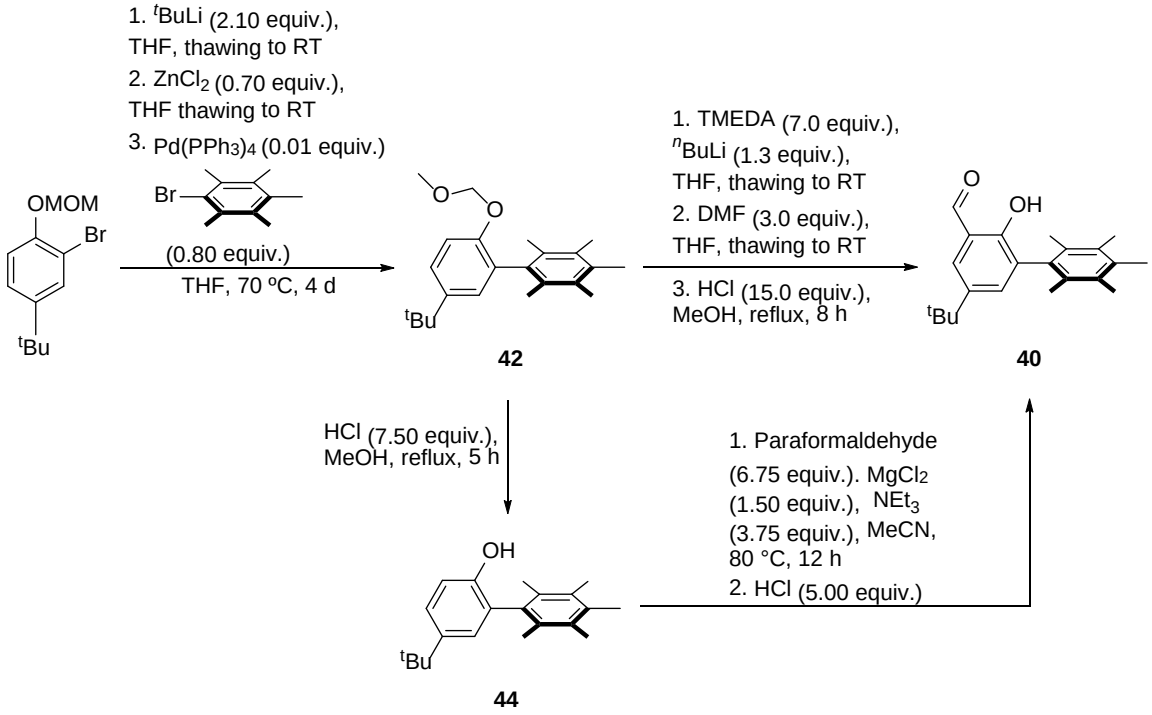
In this hypothesized mechanism, a growing Cr metallocycle would be influenced by the presence of a tethered Cr center (Figure A.2) bound to ethylene or a second

metallocycle. Elimination is envisioned to afford α-olefin as a single product or a smaller distribution than the pseudo Shulz-Flory distribution afford by the example reported by Gibson *et al.*

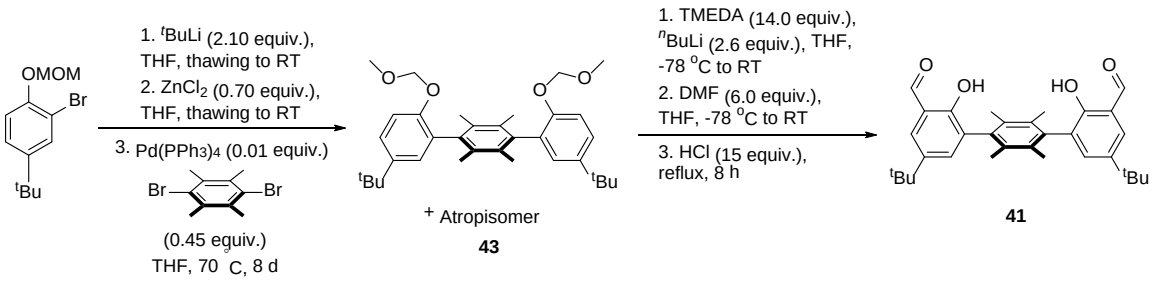
RESULTS & DISCUSSION

Salicylaldehyde **40**[9b] (Scheme A.1) and bissalicylaldehyde **41**[10] (Scheme A.2) were synthesized accorded to literature procedures. Neigishi coupling of bromo-4-(*tert*-butyl)-1-(methoxymethoxy)benzene and bromo-pentamethylbenzene or 1,4-dibromo-tetramethylbenzene afforded the desired biphenyl compound **42** and terphenyl compound **43**. *ortho*-Formylation installs the aldehyde moieties in both cases.

Scheme A.1. Synthesis of Salicylaldehyde 40.



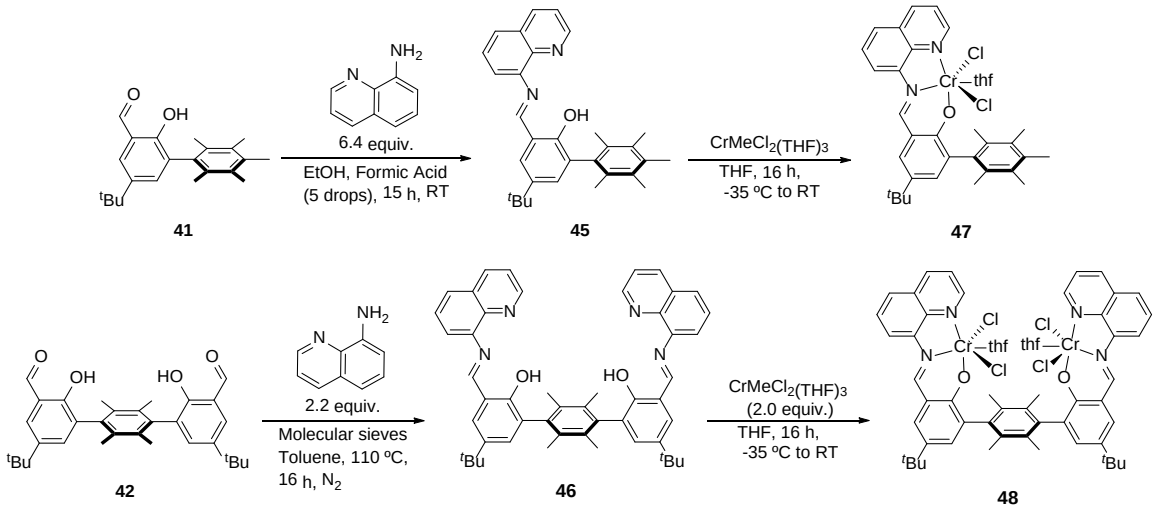
Scheme A.2. Synthesis of Bissalicylaldehyde 41.



An alternative strategy was explored for the preparation of **40** through treatment of alcohol **44** with paraformaldehyde, $MgCl_2$, and NEt_3 in CH_3CN and provided the desired salicylaldehyde in good yield. This strategy is anticipated to be relevant for the preparation of bissalicyladehyde **41**.

Condensation of **40** and **41** with 8-aminoquinoline afforded desired iminophenoxyquinoline compounds **45** and **46**. Both heating in toluene in the presence of molecular sieves and refluxing in EtOH were effective in generating the desired proligands. A color change from orange to dark red was observed upon treatment of these iminophenoxyquinolines with $CrMeCl_2(THF)_3$[12] in THF. The putative Cr compounds were subsequently tested for oligomerization and polymerization activity in the presence of Al activator and pressure of C_2H_4 with Dr. Gyeongshin Choi (Table A.1). The triphenylsilyl-substituted compound **49**, prepared in our group by Dr. Choi, was tested due to similiarity to the reported triptycenyl compound **39**.

Scheme A.3. Synthesis of Phenoxyiminoquinoline Cr Complexes 47 and 48.



Stirring a solution of **49** in a Fischer-Porter vessel with a total volume of 10 mL of toluene and modified methylaluminoxane (MMAO, 100 equiv.) in heptane in the presence of C_2H_4 (60 PSI) at 25 °C for 1 h afforded only 23 mg of insoluble polyethylene (Table A.1, Entry 1). No α-olefins were detected by gas chromatography or mass spectrometry (GC or GC-MS) In contrast, compound **39** is reported in the literature to afford 98.9% α-olefin with an activity of 7450 $mg \cdot \mu mol^{-1} \cdot h^{-1} \cdot bar^{-1}$ (Table A.1). Activation of pre-catalyst **39** was accomplished through treatment with 2200 equiv. of a 10% solution of methylaluminoxane (MAO) in toluene.[8c] To test if the activity of **49** could be increased by changing the activation protocol, the experiment was repeated with pressurization with C_2H_4 followed by injection of MMAO solution in heptane via needle and syringe (Entry 2). In this experiment, only 12 mg of polymer was observed.

MAO was then tested under the catalytic conditions, given the literature precedent. MAO composition is known to vary with age and method of preparation.[13] Volatiles were removed from a 30% MAO solution in toluene under reduced pressure and the resulting powder was dried under reduced pressure at 110 °C. This powder was added to a solution of **49** in toluene in a Fischer-Porter vessel which was allowed to stir for *ca.* 15 min. before being pressurized with C_2H_4 (Entry 3). Gratifyingly, an order of magnitude increase in activity was observed – 627 mg of insoluble polyethylene was observed and trace amounts of a distribution (C_{10} – C_{24}) of α-olefin was observed. The activity of **49** in this reaction is still an order of magnitude less than that reported for compound **39**. It is worth noting that use of MAO in toluene solution may result in oligomerization with activity comparable to that reported for **39**. In

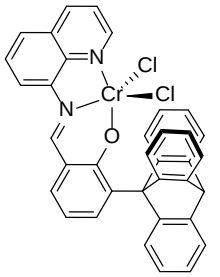
addition, synthesis of **39** and testing under identical reaction conditions is envisioned to aid in optimization of reaction conditions to provide higher activities.

Reaction condition were explored with **49** and solid MAO activator to screen for conditions which increase activity. The amount of MAO was doubled (600 equiv., Entry 4) given the literature precedent (2000 equiv.). The temperature was doubled (50 °C) to possibly encourage elimination of growing alkyl chains or metallocycles, depending on the operative mechanism (Entry 5). Decreasing the C_2H_4 pressure by a quarter was envisioned to slow the rate of alkyl chain or metallocycle growth, possible allowing for increased elimination, although activity was anticipated to suffer (Entry 6). No significant increase in activity was observed. A distribution of α-olefins (C_{10} – C_{24}) was observed with increased MAO loading and temperature. Low activity comparable to experiments with MMAO were observed with decreased ethylene pressure, and no α-olefins could be observed at the decreased pressure.

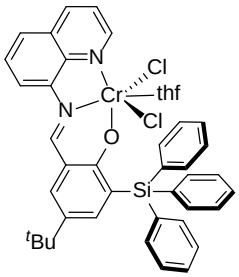
Given that a significant activity increase was not observed after changing MAO loading, temperature, or pressure, initial reaction conditions for oligomerization/polymerization reacts were pursued with compounds **47** and **48** (Entries 7 & 8) to provide evidence for a bimetallic effect on product distribution. With compound **47**, activity was on the same order of magnitude as for **49** (Entry 7). However, α-olefins were not observed by GC-MS with the less bulky pentamethyl phenyl group. With compound **48**, an activity increase was observed and oligomers could be detected by GC-MS. In this reaction, signals consistent with C_{10} - C_{32} products were detected. These data provide initial evidence of an effect of the tethered second phenoxyiminoquinoline moiety on oligomerization and polymerization activity.

Comparison of activity of **39** under the same reaction conditions is necessary to determine if the relatively lower activity is due to experimental conditions or inherent to the structure of compounds **47 - 49**. If activities can be increased, a 1:1 C_2H_4:C_2D_4 mixture can be used to determine if a metallocyclic mechanism is operative.

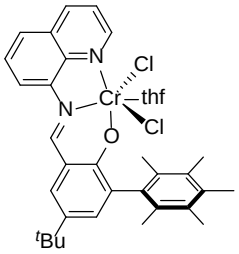
Table A.1. Oligomerization/Polymerization of Phenoxyiminoquinoline Cr compounds 47-49.



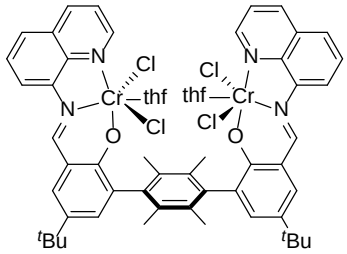
39[a]



49



47



48

run	cat	p (psi)	T (ºC)	activator	equiv. of activator[b]	insoluble polymer (mg)	α-olefin[c]	acitivity (mg/μmol Cr•h•bar)
n/a	**39**[a]	58	50	MAO	2200		98.9%	7450
1	**49**	60	25	**MMAO**	100	23	–	*ca.* 1
2[d]	**49**	60	25	**MMAO**	100	12	–	*ca.* 1
3	**49**	60	25	**MAO**	300	627	C_{10} ~ C_{24}	*ca.* 50[f]
4	**49**	60	25	MAO	**600**	354	C_{10} ~ C_{24}	*ca.* 30[f]
5	**49**	60	**50**	MAO	300	431	C_{10} ~ C_{24}	*ca.* 40[f]
6	**49**	**15**	25	MAO	300	34	–	*ca.* 10
7	**47**	60	25	MAO	300	357	–	*ca.* 30
8[e]	**48**	60	25	MAO	200	1652	C_{10} ~ C_{32}	*ca.* 150[f]

Reaction conditions: toluene (10 mL), 3 μmol catalyst, 1 h, Fischer-Porter vessel. Catalyst was treated by MAO or MMAO before pressurization of Fischer-Porter vessel with ethylene. [a] Reported by Gibson *et al.* Organometallics **2009**, *28*, p. 7033.[8d] [b] Based on Cr. [c] Detected by GC and GC-MS. [d] MMAO was added under ethylene pressure. [e] 1.5 μmol catalyst was used. [f] Estimated by comparison of GC-MS peak height of adamantane peaks to oligomer peaks. Calibration curves were not calculated; oligomer yield is approximate.

If a metallocycle mechanism is operative, extension of the tether from a tetraphenyl linker to an anthracenyl linker may prevent expansion of these metallocycle to afford a wide distribution of oligomers (e. g., C_{10} – C_{32}). Substitution[14] at the 2-position of 8-aminoquinoline has been reported and may also inhibit metallocycle expansion. Increasing steric bulk may be effective in the generation of a smaller distribution of oligomers regardless of whether or not a metallocyclic mechanism is operative.

CONCLUSIONS:

Phenoxyiminoquinoline proligands were prepared for use in Cr-catalyzed olefin oligomerization. Metallation with $CrMeCl_2(THF)_3$ afforded several new compounds. Ethylene oligomerization and polymerization activity (*ca.* 500 $mg \cdot \mu mol^{-1} \cdot h^{-1} \cdot bar^{-1}$) was detected using solid MAO as activator. An order of magnitude decrease in oligomerization and polymerization activity was observed by changing activator (MAO to MMAO) or reducing pressure (60 to 15 PSI). Activities are an order of magnitude lower than those reported for a reported triptycenyl-substituted phenoxyiminoquinoline system reported to be 98.9% selective for generation of a pseudo Schulz-Flory distribution of α-olefins. Preparation of a novel dichromium compound supported by a rigid terpenyl linker was envisioned to afford a precatalyst that would limit metallocycle growth in ethylene oligomerization and afford α-olefins with high selectivity. Use of a putative bimetallic phenoxyiminoquinoline Cr compound resulted in higher activity but a distribution of oligomers (C_{10} – C_{32}) was observed. Changing of activator (MAO in toluene is reported) and testing the experimental setup with the related triptycenyl-substituted phenoxyiminoquinoline Cr compound is anticipated to allow for optimization of oligomerization activity for the newly synthesized compounds. If activity of compounds compares with reported examples under optimized conditions, introduction of increased steric bulk through substitution of the 2-position of the quinoline ring or use of an extended linker between phenoxyiminoquinoline donors (e.g., napthyl or anthracenyl) may facilitate elimination of oligomers of specific carbon length, engendering selectivity desired in the oligomerization reaction.

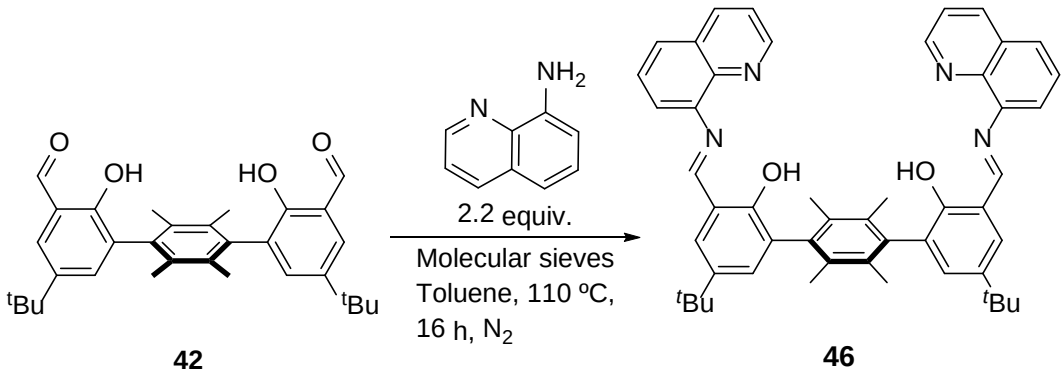
EXPERIMENTAL SECTION:

General considerations

Unless otherwise indicated, reactions performed under inert atmosphere were carried out in oven-dried glassware in a glovebox under a N_2 atmosphere purified by circulation through RCI-DRI 13X-0408 Molecular Sieves 13X, 4x8 Mesh Beads and BASF PuriStar® Catalyst R3-11G, 5x3 mm (Research Catalysts, Inc.). Manipulations were conducted in a N_2-filled glovebox or using standard Schlenk technique under N_2 unless otherwise specified. 2-bromo-4-(*tert*-butyl)phenol[15], 1,4-bis(2'-hydroxyl-3'-formyl-5'-*tert*-butyl)-tetramethylbenzene (**42**),[10] 3-pentamethylphenyl-5-*tert*-butyl-2-hydroxyl-benzaldehyde (**41**),[9b] 1-bromo-2,3,4,5,6-pentamethylbenzene[16] and $CrCl_2Me(THF)_3$[12] were synthesized according to literature procedure. 2-bromo-4-(*tert*-butyl)-1-(methoxymethoxy)benzene was synthesized from 2-bromo-4-(*tert*-butyl)phenol through protection with chloromethyl methyl ether[17] and matched previously reported spectra.[9b] (CAUTION: Chloromethyl methyl ether is highly toxic and a known carcinogen.) 1-Iminoquinolyl-3-tert-butyl-5-triphenylsilyl-phenol was synthesized by Dr. Gyeongshin Choi from 2,6-dibromo-4-(*tert*-butyl)phenoxy)triphenylsilane, which has been previously reported.[18] Retro-Brook rearrangement affords a phenol which can be elaborated to the desired salicylaldehyde and phenoxyiminoquinoline in a similar fashion to the procedures outlined below. Alumina and 3 Å molecular sieves were activated by heating under vacuum at 200 °C for at least 12 h prior to use. Polymer-grade C_2H_4 was purchased from Gas Innovations. Modified methaluminoxane (MMAO: 7 wt. % in heptane) was purchased from Akzo Nobel. Methylaluminoxane (MAO: 30% in toluene) was purchased from Albemarle Corp. ^1H and ^{13}C NMR spectra were recorded on Varian or Bruker spectrometers at ambient temperature unless

denoted otherwise. Chemical shifts are reported with respect to internal solvent for ^{1}H and ^{13}C NMR data, respectively: 7.26 ppm and 77.16 ppm ($CDCl_3$).[19] Analysis of reactions by gas chromatography (GC) was performed on an Agilent 6890N instrument using a flame ionization detector and DB-1 capillary column (10 m length, 0.10 mm diameter, 0.40 μm). Analysis of reactions by gas chromatograph mass spectrometry (GC-MS) was performed on an Agilent 6890 instrument equipped with an HP-5MS 30 m x 0.25 mm x 0.50 μm capillary column (Agilent). The GC was interfaced to an Agilent 5973N mass selective detector.

Synthesis of 1,4-bis(3'-iminoquinolyl-2'-hydroxyl--5'-tert-butyl)-tetramethylbenzene (46).



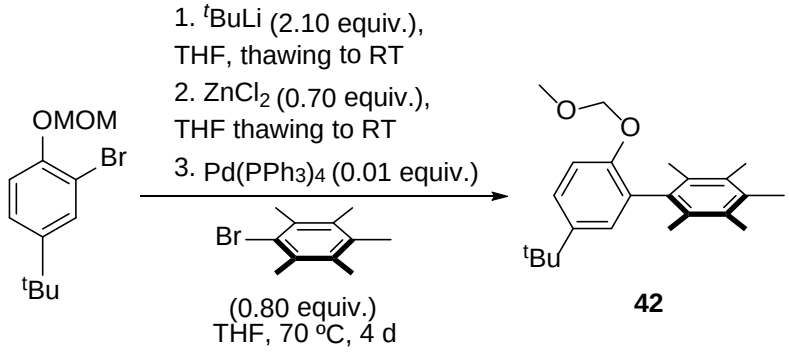
42 **46**

A 100 mL Schlenk tube fitted with a Teflon screw cap was charged with a stir bar, heated in an oven for 1 h, and evacuated on a Schlenk line and allowed to cool to room temperature. The vessel was charged with 1,4-bis(2'-hydroxyl-3'-formyl-5'-*tert*-butyl)-tetramethylbenzene (**42**: 0.130 g, 0.267 mmol, 1.0 equiv.) and 8-aminoquinoline (0.085, 0.588 mmol, 2.2 equiv.) using Schlenk technique and the reaction vessel was place under vacuum for 1 h. The Schlenk tube was sealed and brought into a N_2-filled dry box. In the glovebox, 10 mL toluene and a number of molecular sieves sufficient to cover the bottom of the Schlenk tube. The Schlenk

tube was removed from the glovebox and placed in an oil bath preheated to 110 °C. The reaction vessel was heated for 16 h. After 16 h, the reaction vessel was cooled to room temperature. Volatiles were removed under reduced pressure to afford an orange residue. The Schlenk tube was brought into the glovebox and the residue was washed thrice with 2 mL portions of pentane, then hexanes, then Et_2O. The resulting orange powder was extracted with toluene and filtered through Celite to afford the desired bisphenoxyiminoquinoline **46** (0.055 g, 0.074 mmol, 27.9%) as an orange powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.09 (s, 1H, imine-*H*), 8.98 (m, 2H, quinoline-*H*), 8.18 (m, 2H, quinoline-*H*), 7.70 (m, 2H, quinoline-*H*), 7.59 – 7.50 (m, 4H, quinoline-*H*), 7.47 (d, 2H, Ar-*H*), 7.44 (m, 2H, quinoline-*H*), 7.38 (d, 2H, Ar-*H*), 2.11 (s, 12H, Ar-C-CH_3), 1.38 (s, 18H, Ar-C-C(CH_3)$_3$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.19 (s, imine-*C*H), 157.19 (s, quinoline-*C*H), 150.46 (s, quinoline-*C*), 145.91 (s, Ar-*C*), 142.38 (s, quinoline-*C*), 141.14 (Ar-*C*-C(CH$_3$)$_3$), 137.28 (s, Ar-*C*), 136.09 (s, quinoline-*C*H), 133.13 (s, Ar-*C*H), 132.62 (s, Ar-*C*-CH$_3$), 130.79 (s, Ar-*C*), 129.36 (s, quinoline-*C*), 127.67 (s, Ar-*C*H), 126.70 (s, quinoline-*C*H), 125.88 (s, quinoline-*C*H), 121.68 (s, quinoline-*C*H), 119.91 (s, quinoline-*C*H), 118.92 (Ar-*C*), 34.31 (s, Ar-C-*C*(CH$_3$)$_3$, 31.67 (s, Ar-C-C(*C*H$_3$)$_3$), 18.17 (s, Ar-C-*C*H$_3$). ^{1}H NMR (400 MHz, C_6D_6) δ 14.56 (s, 2H, -O*H*), 8.80 (s, 2H, imine-C*H*), 8.78 (m, 2H, quinoline-*H*), 7.57 (m, 2H, quinoline-*H*), 7.48 (d, 2H, Ar-*H*), 7.35 (d, 2H, Ar-*H*), 7.29 (m, 2H, quinoline-*H*), 7.16 (m, 4H, quinoline-*H*), 6.77 (m, 2H, quinoline-*H*), 2.30 (s, 12H, Ar-C(CH_3)), 1.31 (s, 18H, Ar-C(CH_3)$_3$). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 165.90 (s, Ar-*C*), 158.27 (s, imine-*C*H), 150.65 (s, quinoline-*C*), 146.15 (s, quinoline-*C*), 143.11 (s, quinoline-*C*), 141.04 (s, -*C*(CH$_3$)$_3$), 138.15 (s, Ar-*C*), 135.59

(s, quinoline-*C*H), 133.04 (s, Ar-*C*), 132.96 (s, Ar-*C*H), 132.06 (s, quinoline-*C*H), 129.48 (s, quinoline-*C*H), 128.04 (obscured by solvent residual, detected by HSQC, Ar-*C*H), 126.58 (s, quinoline-*C*H), 125.99 (s, quinoline-*C*H), 121.76 (s, quinoline-*C*H), 119.61 (s, Ar-*C*), 119.33 (s, Ar-*C*), 34.18 (s, -*C*(CH_3)$_3$), 31.66 (s, -C(*C*H_3)$_3$), 18.50 (s, Ar-C(*C*H_3)). Mass calcd. for $C_{50}H_{50}N_4O_2$: 739.4012. Found: 739.4019, M + H.

Synthesis of 1-pentamethylphenyl-2-methoxymethoxy-5-tert-butyl-benzene (42).

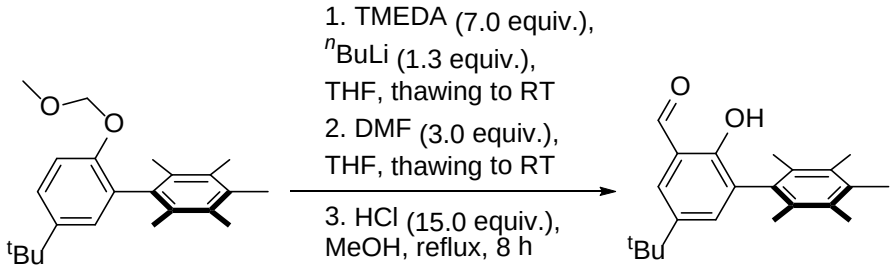


The procedure[10] reported for the preparation of 1,4-bis(2'-hydroxyl-3'-formyl-5'-*tert*-butyl)-tetramethylbenzene was modified to prepare 1-pentamethylphenyl-2-methoxymethoxy-5-tert-butyl-benzene (**42**). In the glovebox, a 500 L Schlenk flask fitted with a Teflon screw cap was charged with a stir bar, 200 mL THF, and 2-bromo-4-(*tert*-butyl)-1-(methoxymethoxy)benzene (18.76 g, 68.7 mmol, 1.00 equiv.). The reaction mixture was frozen in a liquid N_2-chilled cold well. BuLi (9.24 g, 144.2 mmol, 2.10 equiv.) was added portion-wise (*ca.* 1 g/portion) to the stirring, thawing reaction mixture such that frozen solvent was observed at all times during addition. The reaction mixture was chilled in the cold well to maintain the thawing conditions. Upon the completion of addition, the reaction mixture was allowed to warm to room temperature. A light red solution is observed. $ZnCl_2$ (6.56 g, 48.1 mmol, 0.70 equiv.)

was then added as a solid at room temperature. The reaction mixture was allowed to stir for 30 min. A heterogeneous solution was observed. $Pd(Ph_3)_4$ (0.80 g, 0.7 mmol, 0.01 equiv.) and bromo-pentamethylbenzene (12.48 g, 54.9 mmol, 0.80 equiv.) were then added as solids at room temperature. A pale yellow heterogeneous solution was observed. The reaction was stirred in an oil bath pre-heated to 70 °C for 3 d. After 3 d, the Schlenk tube was removed from the oil bath and allow to cool to room temperature. A brown heterogeneous mixture was observed. The reaction mixture was filtered through a coarse fitted funnel packed with Celite. The reaction vessel was washed with 3 portions of CH_2Cl_2 (50 mL) and this organic layer was filtered through Celite and combined with the THF filtrate. Volatiles were removed under reduced pressure using rotary evaporation. The resulting brown residue was extracted with 3 portions of CH_2Cl_2 (100 mL) the combined organics were again filtered through a fritted funnel packed with Celite. This organic layer was washed twice with H_2O (100 mL) and once with brine (100 mL). The organic layer was then dried with $Mg(SO_4)_2$, filtered, and volatiles were removed from the filtrate under reduced pressure using rotary evaportation to afford a brown residue. MeOH was added to the brown residue and the mixture was triturated and sonicated to afford 1-pentamethylphenyl-2-methoxymethoxy-5-tert-butyl-benzene (**42**) in good purity as a white solid with an impurity of bromo-pentamethylbenzene. Sublimation of bromo-pentamethylbenzene from the crude mixture allows for isolation of pure compound **42**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (dd, 1H, Ar-*H*), 7.19 (d, 1H, Ar-*H*), 7.07 (d, 1H, Ar-*H*), 5.08 (s, 2H, $ArOCH_2OCH_3$), 3.37 (s, 3H, $ArOCH_2OCH_3$), 2.34 (s, 3H, $Ar\text{-}C_6(CH_3)_5$), 2.30 (s, 6H, $Ar\text{-}C_6(CH_3)_5$), 2.00 (s, 6H, $Ar\text{-}C_6(CH_3)_5$), 1.33 (s, 9H, $-C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 152.31 (s, Ar-*C*), 144.72 (s, Ar-*C*), 136.72 (s, Ar-*C*), 134.03 (s, Ar-

*C*7), 132.23 (s, Ar-*C*8-10), 132.22 (s, Ar-*C*8-10), 131.70 (s, Ar-*C*8-10), 128.88 (Ar-*C*2 or Ar-*C*3), 124.54 (Ar-*C*5), 114.21 (Ar-*C*2 or Ar-*C*3), 94.44 (s, ArO*C*H2OCH3), 55.78 (s, ArOCH2O*C*H3), 34.32 (s, -*C*(CH3)3), 31.67 (s, -C(*C*H3)3), 18.26 (s, Ar-C6(*C*H3)5), 17.06 (s, Ar-C6(*C*H3)5), 16.80 (s, Ar-C6(*C*H3)5). MS (m/z) calcd. for $C_{23}H_{32}O_2$: 339.2324 (M+H). Found: 339.2319 (FAB+, (M+H)-H2).

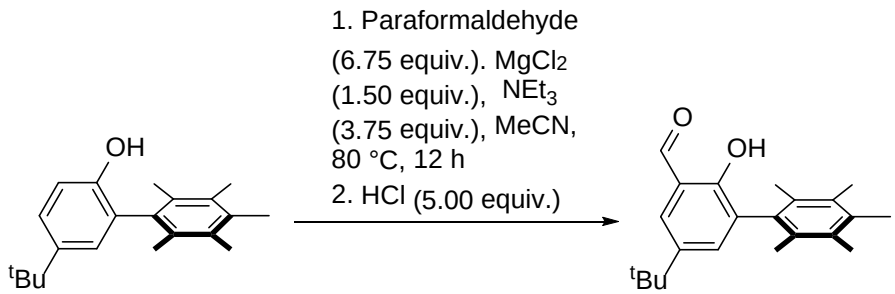
Synthesis of 1-pentamethylphenyl-3-tert-butyl-5-formyl-phenol. (40).



42 **40**

Method A: A 100 mL Schlenk tube fitted with a Teflon screw cap was charged with a stir bar and placed in an oven for 1 h. After 1 h, the Schlenk tube was evacuated on the Schlenk line while cooling to room temperature. Using Schlenk technique, 1-pentamethylphenyl-2-methoxymethoxy-5-tert-butyl-benzene (**42**: 4.290 g, 12.60 mmol, 1.0 equiv.) was added as a solid and placed under vacuum for 3 h. After 3 h, the Schlenk flask was sealed and brought into a N2-filled drybox. THF (40 mL) and tetramethylethylenediamine (10.248 g, 13.1 mL, 88.18 mmol, 7.0 equiv.) were added to the reaction vessel. The mixture was frozen in a liquid N2-chilled cold well. A just-thawed solution of *n*BuLi (6.55 mL of 2.5 M solution in hexanes, 16.38 mmol, 1.3 equiv.) was added dropwise to the thawing reaction mixture. An orange solution was observed with an off-white precipitate. The reaction mixture was allowed to come to room temperature and stir for 2 h. The mixture was again frozen in the cold well. A just-thawed solution of dimethylformamide (2.76 g, 2.91 mL, 37.80 mmol, 3.0 equiv.)

was added to the thawing reaction mixture. The mixture was allowed to come to room temperature and stirred for 12 h. A pale yellow solution was observed. The reaction mixture was transferred to a round bottom flask and volatiles were removed under reduced pressure via rotary evaporation to afford a pale yellow resiude. MeOH (100 mL), HCl (conc. HCl, nominally 12 M, 15.7 mL, 188.98 mmol, 15.0 equiv.), and a stir bar were added to the residue. A reflux condenser was affixed and the mixture was refluxed for 5 h. The reaction was concentrated to afford a precipitate. Filtrate and washing with MeOH afforded the desired salicylaldehyde 1-pentamethylphenyl-3-tert-butyl-5-formyl-phenol (**40**: 1.150 g, 3.54, 28.1%) as a white solid. NMR data matched previously spectra.[9b]

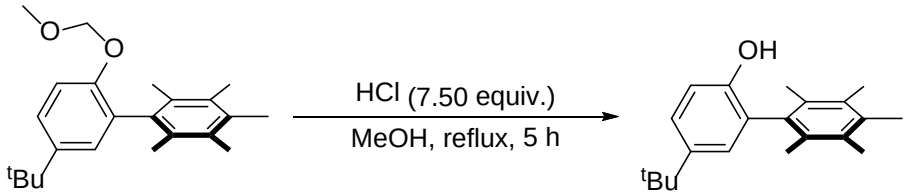


44 **40**

Method B: A procedure reported by Skattebøl and co-workers[20] for the *ortho*-formylation of phenols was used for preparation of salicylaldehyde **40**. A 100 mL Schlenk tube fitted with a Teflon screw cap was charged with a stir bar and placed in an oven for 1 h. After 1 h, the Schlenk tube was evacuated on the Schlenk line while cooling to room temperature. Using Schlenk technique, 1-pentamethylphenyl-3-tert-butyl-phenol (**44**: 1.379 g, 4.65 mmol, 1.00 equiv.; for preparation, see below) was added as a solid and the reaction vessel was evacuated for 3 h. The Schlenk flask was sealed and brought into the glovebox. Paraformaldehyde (0.943 g, 31.40 mmol, 6.75

equiv.), $MgCl_2$ (0.455 g, 6.98 mmol, 1.50 equiv.) NEt_3 (1.765 g, 2.4 mL, 17.45 mmol, 3.75 equiv.), and MeCN (10 mL) were added. The Schlenk tube was removed from the glovebox and placed in an oil bath pre-heated to 80 °C for 12 h. After 12 h, the mixture was removed from heating and allow to cool to remove temperature. The reaction mixture was quenched with HCl (1.94 mL, conc. HCl, nominally 12 M, 23.25 mmol, 5.00 equiv.). Volatiles were removed under reduced pressure via rotary evaporation. Column chromatography using 95:5 hexanes:EtOAc ($R_f \approx 0.3$) affords 1-pentamethylphenyl-3-tert-butyl-5-formyl-phenol (**40**, 1.123 g, 3.46 mmol, 74.4%) as a white solid.

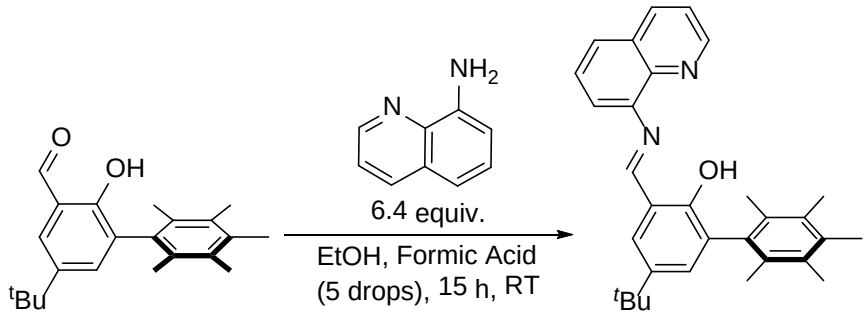
Synthesis of 1-pentamethylphenyl-3-tert-butyl-phenol (44).



42 **44**

A 100 mL round bottom flask was charged with 1-pentamethylphenyl-2-methoxymethoxy-5-tert-butyl-benzene (**42**: 5.000 g, 16.86 mmol, 1.00 equiv.; MeOH precipitate with impurity of bromopentaphenylbenzene), HCl (10.5 mL, conc. HCl, nominally 12 M, 252.97 mmol, 7.50 equiv.), MeOH (100 mL) and a stir bar. The mixture was refluxed for 5 h. Volatiles were removed under reduced pressure via rotary evaporation. Column chromatography using 4:1 hexanes:CH_2Cl_2 as eluent afforded 1-pentamethylphenyl-3-tert-butyl-phenol (**44**) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (dd, 1H, Ar-*H*), 7.01 (d, 1H, Ar-*H*), 6.91 (d, 1H, Ar-*H*), 4.49 (s, 1H, Ph-O*H*), 2.31 (s, 3H, Ar-C-C*H*$_3$), 2.27 (s, 6H, Ar-C-C*H*$_3$), 1.97 (s, 6H, Ar-C-C*H*$_3$), 1.29 (s, 9H, -C(C*H*$_3$)$_3$).

Synthesis of 1-iminoquinoline-3-tert-butyl-5-pentamethylphenyl--phenol (45).

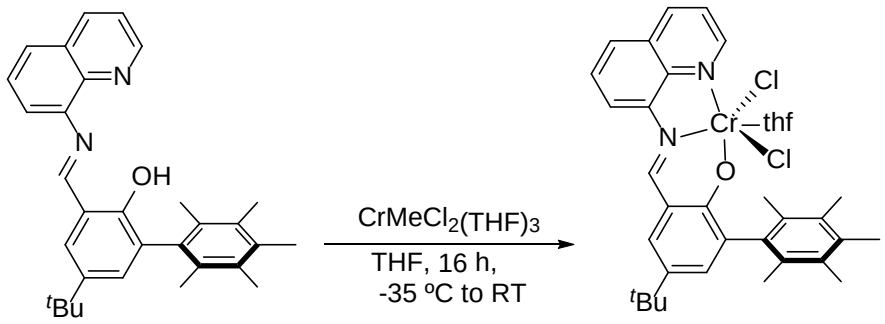


41 **45**

A 100 mL round bottom flask was charged with 1-pentamethylphenyl-3-tert-butyl-5-formyl-phenol (**41**: 0.350 g, 1.080 mmol, 1.0 equiv.), 8-aminoquinoline (1.000 g, 6.936 mmol, 6.4 equiv.), and EtOH (10 mL). Formic acid (5 drops) was added and the resulting mixture was stirred at room temperature for 15 h. An orange precipitate was observed. The precipitate was isolated on a fritted glass funnel washed with a large volume of EtOH to afford 1-iminoquinoline-3-tert-butyl-5-pentamethylphenyl--phenol (**45**: 0.308 g, 0.684 mmol, 63.4%) as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.64 (s, 1H, -O*H*), 9.10 (s, 1H, imine-*H*), 8.93 (m, 1H, quinoline-*H*), 8.18 (m, 1H, quinoline -*H*), 7.70 (m, 1H, quinoline -*H*), 7.56 (m, 1H, quinoline -*H*), 7.51 (m, 1H, quinoline -*H*), 7.45 (d, 1H, Ar-*H*), 7.44 (m, 1H, quinoline -*H*), 7.27 (d, 1H, Ar-*H*), 2.30 (s, 3H, Ar-C(C*H*$_3$)), 2.28 (s, 6H, Ar-C(C*H*$_3$)), 2.05 (s, 6H, Ar-C(C*H*$_3$)), 1.35 (s, 9H, Ar-C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$) δ 166.04 (s, imine-*C*H), 156.92 (s, Ar-*C*), 150.37 (s, quinoline-*C*H), 145.76 (s, quinoline-*C*), 142.41 (s, quinoline-*C*), 141.44 (s, Ar-*C*-C(CH$_3$)$_3$), 136.14 (s, quinoline-*C*H), 135.41 (s, Ar-*C*), 134.49 (s, Ar-*C*-CH$_3$), 132.94 (s, Ar-*C*H), 132.48 (s, Ar-*C*-CH$_3$), 132.37 (s, Ar-*C*-CH$_3$), 130.89 (s, Ar-*C*), 129.36 (s, quinoline-*C*), 127.60 (Ar-*C*H), 126.73 (s, quinoline-*C*H), 126.02 (s, quinoline-*C*H), 121.72 (s, quinoline-*C*H), 119.81 (s, quinoline-*C*H), 118.89 (s, Ar-*C*),

34.26 (s, Ar-*C*(CH$_3$)$_3$), 31.61 (s, Ar-C(*C*H$_3$)$_3$), 18.28 (s, Ar-C(*C*H$_3$), 17.03 (s, Ar-C(*C*H$_3$), 16.90 (s, Ar-C(*C*H$_3$). MS (m/z) calcd. for $C_{31}H_{34}N_2O$: 451.2749 (M+H). Found: 451.2758 (FAB+, (M+H)).

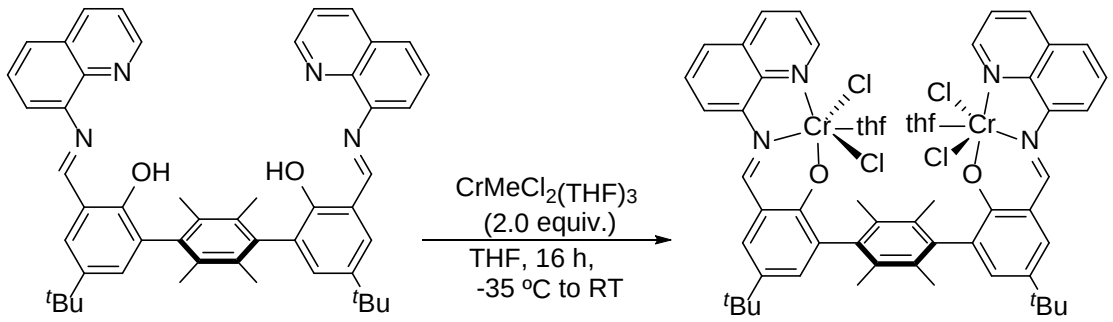
Metallation of 1-iminoquinoline-3-tert-butyl-5-pentamethylphenyl—phenol (45) with CrMeCl$_2$(THF)$_3$ to afford 47.



45 **47**

A 20 mL scintillation vial was charged with a stir bar, THF (3 mL), and phenoxyiminoquinoline (**45**: 0.308 g, 0.68 mmol). An orange homogenous solution was observed. A separate vial was charged with CrMeCl$_2$(THF)$_3$[12] (0.242 g, 0.68 mmol) and THF (2 mL). A light green solution was observed. Both solutions were chilled in a -35 °C freezer. The chilled solution of **45** was added to the chilled solution of CrMeCl$_2$(THF)$_3$ and the reaction mixture was allowed to warm to room temperature. After 1 h, a dark red solution was observed. After 16 h, a red precipitate was observed. Volatiles were removed under reduced pressure to afford a red-brown powder which was used without further purification for C_2H_4 oligomerization/polymerization reactions.

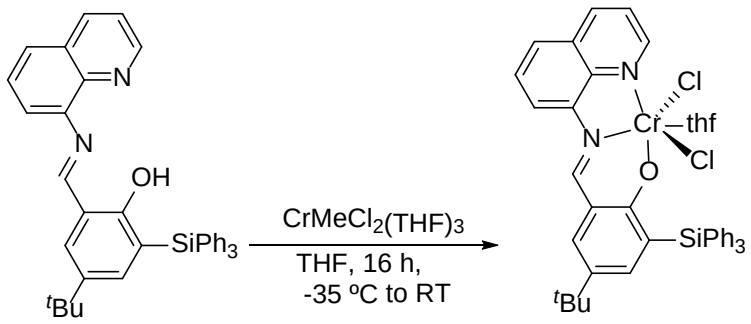
Metallation of 1,4-bis(3'-iminoquinolyl-2'-hydroxyl--5'-tert-butyl)-tetramethylbenzene (46) with $CrMeCl_2(THF)_3$ to afford 48.



46 **48**

A 20 mL scintillation vial was charged with a stir bar, THF (3 mL), and bisphenoxyiminoquinoline (**46**: 0.055 g, 0.07 mmol, 1.0 equiv.). An orange homogenous solution was observed. A separate vial was charged with $CrMeCl_2(THF)_3$[12] (0.053 g, 0.15 mmol, 2.0 equiv.) and THF (2 mL). A light green solution was observed. Both solutions were chilled in a -35 °C freezer. The chilled solution of **46** was added to the chilled solution of $CrMeCl_2(THF)_3$ and the reaction mixture was allowed to warm to room temperature. After 1 h, a dark red solution was observed. After 16 h, a red precipitate was observed. Volatiles were removed under reduced pressure to afford a red-brown powder which was used without further purification for C_2H_4 oligomerization/polymerization reactions.

Metallation of 1-iminoquinoline-3-tert-butyl-5-triphenylsilyl-phenol with $CrMeCl_2(THF)_3$ to afford 49.



49

A 20 mL scintillation vial was charged with a stir bar, THF (3 mL), and 1-Iminoquinolyl-3-tert-butyl-5-triphenylsilyl-phenol (0.093 g, 0.17 mmol). An orange homogenous solution was observed. A separate vial was charged with $CrMeCl_2(THF)_3$[12] (0.059 g, 0.17 mmol) and THF (2 mL). A light green solution was observed. Both solutions were chilled in a -35 °C freezer. The chilled solution of phenoxyiminoquinoline was added to the chilled solution of $CrMeCl_2(THF)_3$ and the reaction mixture was allowed to warm to room temperature. After 1 h, a dark red solution was observed. After 16 h, a red precipitate was observed. Volatiles were removed under reduced pressure to afford a yellow-brown powder which was used without further purification for C_2H_4 oligomerization/polymerization reactions.

Oligomerization/Polymerization Procedure A: MMAO Activator.

A Fischer-Porter vessel was charged with a stir bar heated in an oven for 8 h and introduced into the glovebox. A Fischer-Porter reactor top/regulator was introduced into the glovebox after being placed under dynamic vacuum for a minimum of 8 h. In the glovebox, the Fischer-Porter vessel was charged with a solution of phenoxyiminoquinoline Cr compound (3.0 μmol, 1.0 equiv.) and a solution of

MMAO (0.15 mL, 7 wt% Al in heptane, 0.3 mmol, 100.0 equiv.). The reactor was sealed, removed from the glovebox, and place in an oil bath pre-heated to the specified temperature. The Fischer-Porter apparatus was then charged with the desired pressure of C_2H_4 and allowed to stir vigorously for the specific period of time. Typically, *ca.* 15 min. elapsed between addition of activator and pressurization with C_2H_4. After the specified period of time, the reactor was removed from the oil bath, vented to release C_2H_4, and 10 mL of 1 M HCl was added to afford a biphasic mixture. A known mass of adamantane (*ca.* 0.008 g, 0.059 mmol to 0.015 g, 0.110 mmol) was added as a solution in 2 mL toluene. An aliquot was then taken from the organic (top) layer of the biphasic mixture for quantification of 1-hexene or 1-octene production by GC and identification of higher oligomers by GC-MS.

Oligomerization/Polymerization Procedure B: Solid MAO Activator.

"Oligomerization/Polymerization Procedure A" (above) was followed except for choice of activator. Solid MAO (0.052 g, 0.3 mmol, 300 equiv.) was added to a 10 mL solution of phenoxyiminoquinoline Cr compound (0.002 g, 3.0 μmol, 1.0 equiv.) in the glovebox (no MMAO was used). The rest of "Procedure A" was then followed.

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