Supporting Information for

Stoichiometrically-Activated Catalysts for Ethylene Tetramerization using Diphosphinoamine-Ligated Cr Trishydrocarbyl Complexes

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Table of Contents

General Considerations

All synthetic procedures containing chromium were performed in a nitrogen-atmosphere glove box or in sealed containers under a stream of nitrogen gas. All glassware was oven-dried and kept under active vacuum prior to use. Diethyl ether, tetrahydrofuran (THF), toluene, and pentane solvents were purified by sparging with nitrogen and then passing through a column of activated A2 alumina into sealed containers, degassed under active vacuum and stored over activated molecular sieves prior to use. C_6D_6 (Cambridge Isotope Laboratories) and 1,4-dioxane were dried over Na/benzophenone, vacuum distilled and kept over activated molecular sieves prior to use. Chlorobenzene was distilled from CaH_2, stored over activated molecular sieves for at least 24 hours, and filtered through activated alumina directly before use. Chlorobenzene-d_5 (from Acros Organics) was degassed using three freeze-pump-thaw cycles and stored over molecular sieves prior to use. M-MAO 3A was purchased from AkzoNobel as a 7% w/w Al solution in heptane. Ethylene gas was purchased at polymer purity (99.9%) from Matheson, and was dried by passage through two 1L Swagelok steel columns packed with 3Å activated molecular sieves and Mn(II) oxide on vermiculite.[1] $CrCl_3(THF)_3$ was synthesized according to the literature procedure, using $CrCl_3$ (anhydrous) purchased from Strem.[2] The synthesis of ^{iPr}PNP, ^{tol}PNP, and $[H(Et_2O)_2][BAr'_4]$ have been previously reported.[3-5] $CrPh_3(THF)_3$ and bis(2-bromobenzyl)ether were synthesized according to the reported literature procedures.[6,7] Cr(*p*-tol)$Cl_2(THF)_3$ was synthesized according to the literature procedure,[8] and Cr(Me)$Cl_2(THF)_3$ was synthesized according to a modification of this procedure using MeMgBr. NMR spectra were recorded on a Varian 300 MHz or 400 MHz Spectrometer. Gas chromatography (GC) was performed on an Agilent 6890A instrument using a DB-1 capillary column (10 m length, 0.10 mm diameter, 0.40 μm film) and a flame ionization detector. Gas chromatography/mass spectrometry (GC-MS) was performed on an Agilent 6890A instrument using a HP-5MS column (30 m length, 0.25 mm diameter, 0.50 µm film) and an Agilent 5973N mass-selective EI detector.

Synthetic Protocols

Preparation of Mg(*o*-$C_6H_4CH_2)_2O$. A solution of bis(2-bromobenzyl)ether was prepared in Et_2O (0.02 to 0.05 M). This was stirred in the presence of excess activated magnesium turnings for 12 to 18 h, until a yellow solution formed and a quenched aliquot indicated complete consumption of the starting material by GC/MS (pure dibenzylether). Then, the solution was decanted from the Mg turnings, and the volume was doubled by addition of THF. Subsequently, 1,4-dioxane (1 to 2 v/v%) was added, causing the precipitation of white solids (magnesium bromide salts). The yellow solution of $Mg(O(CH_2C_6H_4)_2$ was filtered, using a small amount of Et_2O to rinse, and used directly in further reactions.

Cr((*o*-$C_6H_4CH_2)_2O$)(*p*-tol)(THF)$_2$ (1). Bisarylether magnesium reagent Mg(*o*-$C_6H_4CH_2)_2O$ (5.38 mmol) was prepared in 150 mL 1:1 Et_2O:THF, with 2 mL 1,4-dioxane. This solution was added dropwise to a solution of Cr(*p*-tol)$Cl_2(THF)_3$ (2.32g, 5.38 mmol) dissolved in 60 mL 1:1 Et_2O:THF, with 2 mL 1,4-dioxane over 30 min at -78°C. The resulting green suspension was stirred at -78 °C for 1h, then warmed to 0 °C over 2 h. The resulting dark red solution was allowed to warm to RT, stirring for 17 h. The dark red solution was filtered from white precipitate, and reduced in vacuo to 12 mL. To this, 24 mL pentane was added to precipitate bright red solids. These were dissolved in THF, from which red crystals of **1** were grown at -35 °C over several days; the product was dried under vacuum after decanting the solvent (0.687 g, 26% yield). In C_6D_6: $\mu_{eff} = 2.9(1)\ \mu_B$ (average of three measurements). In C_6D_6 + 100 THF: $\mu_{eff} = 3.8\ \mu_B$. Anal. Calcd. for $C_{29}H_{35}CrO_3$: C, 72.03; H, 7.30; N, 0.00. Found: C, 71.63; H, 7.32; N, 0.01.

Cr((*o*-$C_6H_4CH_2)_2O$)(Me)(THF)$_2$. (2) Bisarylether magnesium reagent Mg(*o*-$C_6H_4CH_2)_2O$ (1.99 mmol) was prepared in 100 mL 1:1 Et_2O:THF, with 1 mL 1,4-dioxane. This solution was added dropwise over 15 min to a -78°C solution of $Cr(Me)Cl_2(THF)_3$ (0.706 g, 1.99 mmol) dissolved in 40 mL 1:1 Et_2O:THF, with 1.5 mL 1,4-dioxane. The resulting red/brown solution was stirred for a further 1 h, then warmed to RT over 15 h. The red solution was filtered from white solids, and reduced in vacuo to 12 mL. To this, 24 mL pentane was added to precipitate dark solids from the red solution. This mixture was filtered, and the solids were discarded. Dark red crystals were obtained by cooling the filtrate to -35 °C for two weeks, and were redissolved into THF for a second recrystallization. Red crystals of **2** were grown at -35 °C by diffusion of pentane into the THF filtrate; the product was obtained by decantation, and dried under vacuum (0.291 g, 36% yield). In C_6D_6: $\mu_{eff} = 2.1\ \mu_B$. In C_6D_6 + 100 THF: $\mu_{eff} = 3.9\ \mu_B$. Anal. Calcd. for $C_{23}H_{31}CrO_3$: C, 67.79; H, 7.67; N, 0.00. Found: C, 67.80; H, 8.00; N, 0.07.

Synthesis of (^{tol}PNP)Cr((*o*-$C_6H_4CH_2)_2$O)(*p*-tol). (3) A solution of ^{tol}PNP (0.096 g, 0.20 mmol) in 3 mL C_6H_6 was used to dissolve compound **1**, which was a dry red crystalline powder (0.098 g, 0.20 mmol). The resulting green solution was stirred for five minutes, then lyophilized down to a dry orange/brown powder. The crude product was dissolved in 2 mL toluene and layered with 12 mL pentane and cooled to -35°C for 8 days. Brown microcrystalline **3** was obtained by decanting the supernatant, and the product was dried under vacuum (0.077 g, 0.094 mmol, 47% yield). Single, brown crystals of **3** suitable for XRD were grown by cooling a very dilute, green solution of crude **3** in pentane to 35°C (if the solution was too concentrated, the product was observed to precipitate out within several minutes). In C_6D_6: $\mu_{eff} = 3.8\ \mu_B$. Anal. Calcd. for $C_{52}H_{46}CrNOP_2$: C, 76.64; H, 5.69; N, 1.72. Found: C, 76.26; H, 5.81; N, 1.33.

Synthesis of (^{tol}PNP)Cr((*o*-$C_6H_4CH_2)_2$O)(Me). (4) A solution of ^{tol}PNP (0.091 g, 0.19 mmol) in 2 mL C_6H_6 was used to dissolve compound **2**, which was a dry red/brown crystalline powder (0.078 g, 0.19 mmol). The resulting brown solution was stirred for ten minutes, then lyophilized down to a dry brown powder. The crude product was dissolved in 2 mL toluene and cooled to -35°C for 2 weeks. The dark brown crystals of **4** were obtained by decantation and dried under vacuum (0.070 g, 0.095 mmol, 49% yield). The same procedure was used to obtain single crystals of **4** suitable for XRD. In C_6D_6: $\mu_{eff} = 3.4\ \mu_{B.}$ Anal. Calcd. for $C_{46}H_{42}CrNOP_2$: C, 74.79; H, 5.73; N, 1.90. Found: C, 75.31; H, 6.09; N, 1.31.

Oligomerization Catalysis

Representative Procedure for Oligomerization Catalysis via Stoichiometric Activation of 1-4. A mixture of **1** (4.0 mg, 0.0080 mmol) and ^{iPr}PNP (3.8 mg, 0.0088 mmol) were dissolved in 1.0 mL PhCl. This was frozen in the glovebox cold well, and a 0.5 mL PhCl solution of $[H(Et_2O)_2][BAr'_4]$ (8.1 mg, 0.0080 mmol) was added dropwise to the thawing solution. After ~30 seconds, the brown solution was diluted to 7.5 mL, then added to a prechilled Fischer-Porter reactor, causing the solution to freeze upon contacting the glass. The reactor was sealed, taken out of the glovebox, and stirred for 5 min in a water bath at 25 °C, then pressurized to 100 psig of ethylene, and stirred for 45 min at 25 °C. The reactor was then vented, and 0.1 mL methanol was added to quench the reaction mixture. The solution was used to dissolve 20 mg adamantane, filtered, and analyzed by GC/FID to quantify the oligomers vs. adamantane. It was also analyzed by GC/MS to identify other organic residues. Polymer was weighed on a tared glass fritted filter.

Representative Procedure for Oligomerization Catalysis using $CrCl_3(THF)_3$ and MMAO. A mixture of $CrCl_3(THF)_3$ (0.0040 g, 0.0080 mmol) and ^{iPr}PNP (3.8 mg, 0.0088 mmol) were dissolved in 6.15 mL PhCl. This was loaded into a glass Fischer-Porter reactor, and sealed in the glovebox. The reactor was taken out of the glovebox, and purged with ethylene at 30 psig for 60 seconds, during which time a solution of MMAO-3A (1.35 mL, 2.4 mmol) was added. The reactor was quickly sealed, and was pressurized to 100 psig of ethylene, and stirred for 45 min at 25 °C. The reactor was then vented, and 10 mL 1M HCl was added to quench the reaction. To the mixture, 20 mg adamantane was added, and the organic layer was separated, filtered, and analyzed by GC/FID to quantify the oligomers vs. adamantane. Polymer was weighed on a tared glass fritted filter.

Table S1. Results of Individual Catalytic Runs (averages shown in Table 1).

Entry	Cr. Source/ PNP	n HBAr'$_4$ / n MMAO	g/g Cr	PE^a	C_6^{a}	1-C_8^{a}	C_{10}^{a}	C_{12}^{a}	C_{14}^{a}	% 1-C_6 in C_6^{a}	1-octene: 1-hexene^b
1a	**1** / ^{iPr}PNP	1 / 0	1700	0.3%	75%	22%	1.4%	1.1%	0.2%	97%	0.22
1b	**1** / ^{iPr}PNP	1 / 0	1500	0.0%	75%	22%	2.1%	1.5%	0.1%	97%	0.23
2a	**2** / ^{iPr}PNP	1 / 0	390	0.0%	76%	21%	2.2%	0.8%	0.2%	97%	0.21
2b	**2** / ^{iPr}PNP	1 / 0	610	0.0%	77%	22%	0.6%	0.6%	0%	97%	0.22
3a	**1** / ^{tol}PNP	1 / 0	1000	0.0%	61%	37%	0.7%	1.1%	0.4%	86%	0.52
3b	**1** / ^{tol}PNP	1 / 0	930	0.0%	62%	36%	0.5%	0.8%	0.1%	87%	0.50
4a	**2**/ ^{tol}PNP	1 / 0	200	0.0%	65%	35%	0.1%	0.1%	0%	88%	0.47
4b	**2**/ ^{tol}PNP	1 / 0	320	0.0%	67%	32%	0.1%	0.3%	0%	88%	0.41
5a	**3** / --	1 / 0	1300	0.0%	48%	46%	2.7%	3.0%	1.0%	79%	0.92
5b	**3** / --	1 / 0	5300	0.4%	44%	40%	4.9%	7.2%	3.0%	72%	0.95
6a	**4** / --	1 / 0	4700	0.4%	43%	40%	5.9%	8.5%	2.8%	76%	0.92
6b	**4** / --	1 / 0	2700	0.8%	44%	47%	2.6%	3.7%	1.8%	75%	1.09
7a	**1** / ^{iPr}PNP	1 / 5	4100	0.5%	46%	38%	5.7%	6.9%	2.7%	91%	0.68
7b	**1** / ^{iPr}PNP	1 / 5	4200	0.5%	48%	35%	6.3%	7.3%	2.8%	92%	0.60
8a	**1** / ^{tol}PNP	1 / 5	2000	0.0%	43%	49%	2.2%	3.5%	1.8%	75%	1.15
8b	**1** / ^{tol}PNP	1 / 5	980	2.4%	48%	47%	0.9%	1.6%	0.6%	80%	0.93
9a	**2**/ ^{tol}PNP	1 / 5	1400	0.0%	59%	38%	0.9%	1.5%	0.3%	85%	0.58
9b	**2**/ ^{tol}PNP	1 / 5	2400	0.0%	46%	46%	2.5%	3.5%	1.5%	77%	0.99
10a	**3** / --	1 / 5	3000	2.1%	44%	41%	4.7%	5.8%	2.2%	79%	0.90
10b	**3** / --	1 / 5	4700	1.3%	41%	39%	6.2%	9.1%	3.4%	78%	0.93
11a	**4** / --	1 / 5	4200	0.9%	55%	32%	4.7%	5.6%	1.5%	86%	0.51
11b	**4** / --	1 / 5	4900	1.0%	41%	40%	6.1%	8.7%	3.4%	77%	0.97
12a	$CrCl_3(THF)_3$ / ^{iPr}PNP	0 / 300	4500	0.2%	43%	43%	4.8%	6.8%	2.6%	89%	0.85
12b	$CrCl_3(THF)_3$ / ^{iPr}PNP	0 / 300	5900	0.5%	43%	39%	6.5%	8.4%	3.1%	89%	0.76
13a	$CrCl_3(THF)_3$ / ^{tol}PNP	0 / 300	3000	0.6%	40%	50%	2.8%	4.4%	2.2%	74%	1.27
13b	$CrCl_3(THF)_3$ / ^{tol}PNP	0 / 300	3200	0.0%	39%	50%	3.1%	4.9%	2.4%	73%	1.30

Conditions: [Cr] = 1 mM, Solvent: 7.5 mL PhCl. Pressure: 100 psig C_2H_4. Temperature: 25°C. Reaction time: 45 min. ^{a} total wt%: attempts to quantify 1-butene were not made. C_{10}-C_{14} are mixtures of branched olefins (co-oligomers). ^{b} molar ratio.

X-Ray Crystallography

Suitable crystals of complexes **1**, **2**, **3**, and **4** were mounted on a nylon loop using Paratone oil, then placed on a diffractometer under a nitrogen stream. X-ray intensity data were collected on a Bruker APEXII CCD area detector or a Bruker D8 VENTURE Kappa Duo PHOTON 100 CMOS detector employing Mo-Kα radiation (λ = 0.71073 Å) or Cu-Kα radiation (λ = 1.54178 Å) at a temperature of 100 K. All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEX3 software.[9] In APEX3, intensity data were absorption-corrected using SADABS, and space groups were determined on the basis of systematic absences and intensity statistics using XPREP. Using Olex2, the structures were solved using ShelXT and refined to convergence by full-matrix least squares minimization.[10,11] All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model. For complex **2**, the positional disorder of the carbon atoms for the aryl and THF ligands in two of the three molecules in the asymmetric unit was modeled using the PART instruction. Graphical representation of structures with 50% probability thermal ellipsoids were generated using Diamond 3 visualization software.[12]

Table S2. Crystal and Refinement Data for Complexes **1** and **2**.

Compound	**1**	**2**
CCDC	1562429	1562430
Empirical formula	$C_{29}H_{35}CrO_3$	$C_{23}H_{31}CrO_3$
Formula weight	483.57	407.48
Temperature/K	100.02	99.99
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$Pna2_1$
a/Å	18.6763(14)	17.0687(6)
b/Å	17.5939(12)	26.5488(10)
c/Å	15.6720(11)	13.6540(6)
α/°	90	90
β/°	106.878(4)	90
γ/°	90	90
Volume/$Å^3$	4927.8(6)	6187.4(4)
Z	8	12
$\rho_{calc}g/cm^3$	1.304	1.312
μ/mm^{-1}	0.492	0.574
F(000)	2056	2604
Crystal size/mm^3	0.39 × 0.367 × 0.366	0.26 × 0.167 × 0.095
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.278 to 75.66	4.900 to 64.998
Index ranges	$-31 \leq h \leq 31$, $-30 \leq k \leq 29$, $-26 \leq l \leq 26$	$-25 \leq h \leq 25$, $-40 \leq k \leq 33$, $-20 \leq l \leq 17$
Reflections collected	194220	76731
Independent reflections	25298 [R_{int} = 0.0538, R_{sigma} = 0.0379]	20045 [R_{int} = 0.0744, R_{sigma} = 0.1018]
Data/restraints/parameters	25298/0/597	20045/1/773
Goodness-of-fit on F^2	1.033	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0452, wR_2 = 0.1171	R_1 = 0.0741, wR_2 = 00.1643
Final R indexes [all data]	R_1 = 0.0734, wR_2 = 0.1339	R_1 = 0.1525, wR_2 = 0.1959
Largest diff. peak/hole / e $Å^{-3}$	1.781/-0.607	1.350/-0.800

Table S3. Crystal and Refinement Data for Complexes **3** and **4**.

Compound	**3**	**4**
CCDC	1562431	1562432
Empirical formula	$C_{57}H_{58}CrNOP_2$	$C_{56.5}H_{54}CrNOP_2$
Formula weight	886.98	876.94
Temperature/K	100.04	100.02
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1$
a/Å	10.5738(7)	13.5452(5)
b/Å	18.1251(13)	14.5414(6)
c/Å	24.8864(17)	23.7385(10)
α/°	90	90
β/°	101.934(5)	96.029(3)
γ/°	90	90
Volume/$Å^3$	4666.4(6)	4649.8(3)
Z	4	4
ρ_{calc}g/cm^3	1.263	1.253
μ/mm^{-1}	2.974	2.981
F(000)	1876	1848
Crystal size/mm^3	0.088 × 0.113 × 0.139	0.084× 0.051× 0.026
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.06 to 148.95	6.562 to 140.966
Index ranges	$-13 \leq h \leq 13$, $-20 \leq k \leq 22$, $-26 \leq l \leq 30$	$-16 \leq h \leq 15$, $-17 \leq k \leq 17$, $-28 \leq l \leq 28$
Reflections collected	43912	48372
Independent reflections	9268 [R_{int} = 0.2153, R_{sigma} = 0.1812]	16960 [R_{int} = 0.1637, R_{sigma} = 0.1980]
Data/restraints/parameters	9268/0/503	16960/46/1080
Goodness-of-fit on F^2	1.072	1.002
Final R indexes [I>=2σ (I)]	R_1 = 0.1299, wR_2 = 0.2288	R_1 = 0.0866, wR_2 = 0.1785
Final R indexes [all data]	R_1 = 0.2107, wR_2 = 0.2638	R_1 = 0.1598, wR_2 = 0.2153
Largest diff. peak/hole / e $Å^{-3}$	0.59/-0.754	0.532/-0.664

Table S4. Selected bond angles and distances for complexes **1** and **2**.

Bond Distance (Å) Averages[a]	**Complex**	
	1	**2**
Cr-C1	2.0664(11)	2.056(5)
Cr-C2	2.0637(11)	2.056(5)
Cr1-C3	2.0557(10)	2.069(5)
Cr1-O1	2.1522(8)	2.181(4)
Cr1-O2	2.1673(8)	2.158(3)
Cr1-O3	2.1794(8)	2.162(3)
Bond Angles (°) Averages[a]		
C1-Cr1-C2	100.06(4)	93.9(3)

[a] Average metrics calculated for two (compound **1**) or three (compound **2**) molecules present in the asymmetric unit.

Table S5. Selected bond angles and distances for complexes **3** and **4**.

Bond Distance (Å) Averages[a]	**Complex**	
	3	**4**
Cr1-C1	2.087(9)	2.032(12)
Cr1-C2	2.060(9)	2.062(12)
Cr1-C3	2.069(8)	2.080(13)
Cr1-P1	2.591(2)	2.493(4)
Cr1-P2	2.538(3)	2.500(3)
Cr1-O1	2.154(6)	2.171(8)
Bond Angles (°) Averages[a]		
C1-Cr1-C2	102.5(4)	105.9(5)
P1-Cr1-P2	65.22(8)	65.48(11)

[a] Average metrics calculated for two (compound **4**) molecules present in the asymmetric unit.

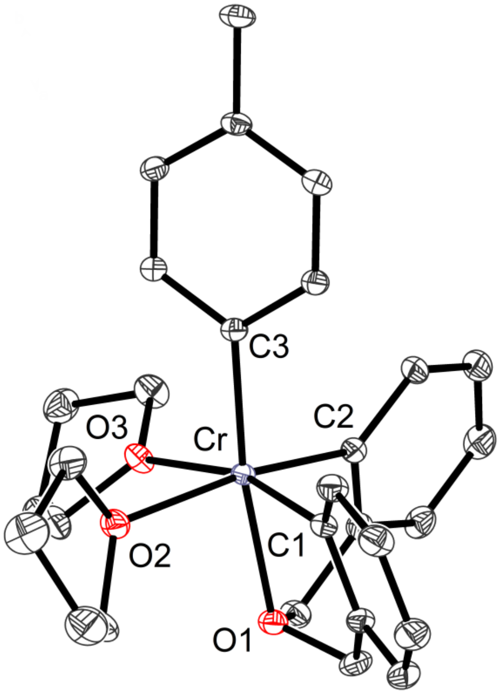

Figure S1. Molecular structure of **1** with thermal ellipsoids at the 50% probability level. Selected bond distances/angle shown in table **S4**. H atoms have been omitted for clarity. There are two molecules in the asymmetric unit, with C1 corresponding to C30, C2 to C31, and C3 to C32. For oxygen, O1 corresponds to O4, O2 to O5, and O3 to O6.

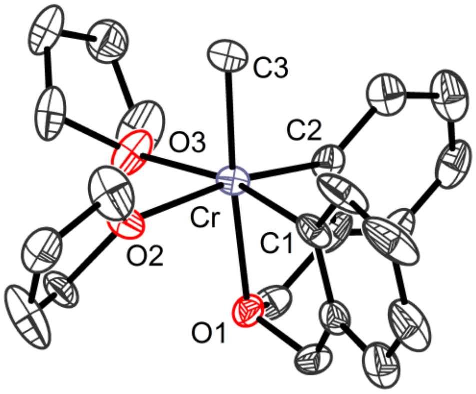

Figure S2. Molecular structure of **2** with thermal ellipsoids at the 50% probability level. Selected bond distances/angle shown in table **S4**. H atoms have been omitted for clarity. There are three molecules in the asymmetric unit, with C1 corresponding to C24 & C47, C2 to C25 & C48, and C3 to C26 & C49. For oxygen, O1 corresponds to O4 & O7, O2 to O5 & O8, and O3 to O6 & O9.

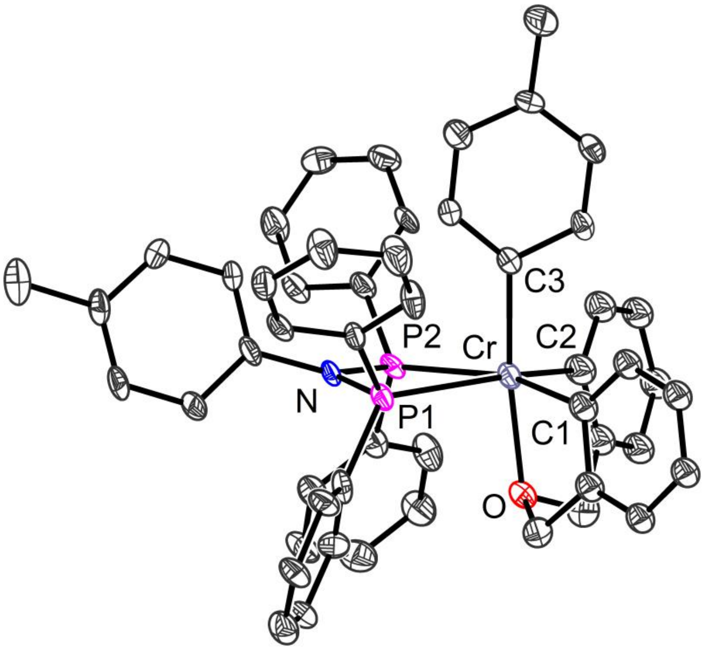

Figure S3. Molecular structure of **3** with thermal ellipsoids at the 50% probability level. H atoms and pentane solvent molecule have been omitted for clarity. Selected bond distances/angle shown in table **S5**.

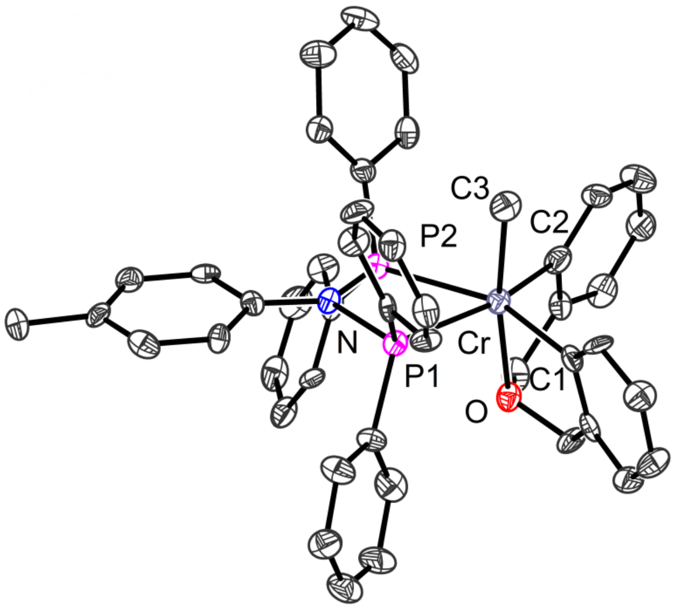

Figure S4. Molecular structure of **4** with thermal ellipsoids at the 50% probability level. Selected bond distances/angle shown in table **S5**. H atoms and toluene solvent molecules have been omitted for clarity. There are two molecules in the asymmetric unit, with C1 corresponding to C47, C2 to C48, and C3 to C49. For phosphorus, P1 corresponds to P3, and P2 to P4.

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