

Supporting Information for

Nickel-Based Heterometallic Catalysts for Ethylene-Acrylate

Copolymerization: Interrogating Effects of Secondary Metal Additives

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1 General Considerations

All air- and water-sensitive compounds were manipulated under N₂ or Ar using standard Schlenk or glovebox techniques. The solvents for air- and moisture-sensitive reactions were dried over sodium benzophenone ketyl or calcium hydride or by the method of Grubbs.¹ Deuterated solvents were purchased from Cambridge Isotopes Lab, Inc.; C₆D₆, and THF-d₈ was dried over a purple suspension with Na/benzophenone ketyl and vacuum transferred; Ethylene (99.999%) for ethylene homopolymerization was purchased from Matheson Tri-Gas and equipped with a PUR-Gas in-line trap to remove oxygen and moisture before use. Tert-butyl acrylate were dried over 4 Å sieves for greater than 72h, vacuum transferred, and passed over an activated alumina plug. Dimethoxybenzene, 1-methoxynaphthalene, and pyridine were dried over calcium hydride and vacuum-transferred or distilled prior to use. Secondary metal precursors were purchased from Sigma-Aldrich and used without further purification. Bis(dimethoxyphenyl)phosphine chloride,² 1,3-dibromo-5-(tert-butyl)-2-(methoxymethoxy)-benzene,³ Nipy₂(CH₂Si(CH₃)₃)₄,⁴ and mononuclear catalyst **1** were synthesized according to literature procedures. All ¹H, ¹³C, and ³¹P spectra of organic and organometallic compounds were recorded on Varian Mercury 300, Varian INOVA-400, or 500, or Bruker Cryoprobe 400 spectrometers. ¹H and ¹³C chemical shifts are reported relative to residual solvent resonances.

2 Binding Studies with Secondary Metal Additives

Conditions for Figure 2

Unless specified, **1**: 4.9 mg, 0.005 mmol; secondary metal additive: 5 equiv., 0.025 mmol; V(total): 0.5 mL. Reaction was performed in toluene, or THF if no reactivity was observed in toluene at elevated temperatures. The mixtures were stirred/rotated at room temperature for 20 min prior to spectra collection unless specified. The $^{31}\text{P}\{^1\text{H}\}$ spectrum of **1** (top spectrum) was collected in toluene and calibrated by an external standard.

a) ZnMe_2 : 0.1 mL, 0.25 M, toluene solvent. The mixture was heated at 50°C for 20 min prior to spectrum collection.

b) AlEt_3 : 0.1 mL, 0.25 M in toluene; toluene solvent.

c) ZnCl_2 : 3.4 mg, 0.025 mmol; toluene solvent.

d) Zn(OMe)_2 : 3.2 mg, 0.025 mmol; THF was used instead of toluene. The mixture was heated at 50°C for 20 min prior to spectrum collection.

e) $\text{Al(O}^i\text{Pr)}_3$: 5.1 mg, 0.025 mmol; toluene solvent. The mixture was heated at 50°C for 20 min prior to spectrum collection.

f) KO^tBu : 2.8 mg, 0.025 mmol; THF was used instead of toluene.

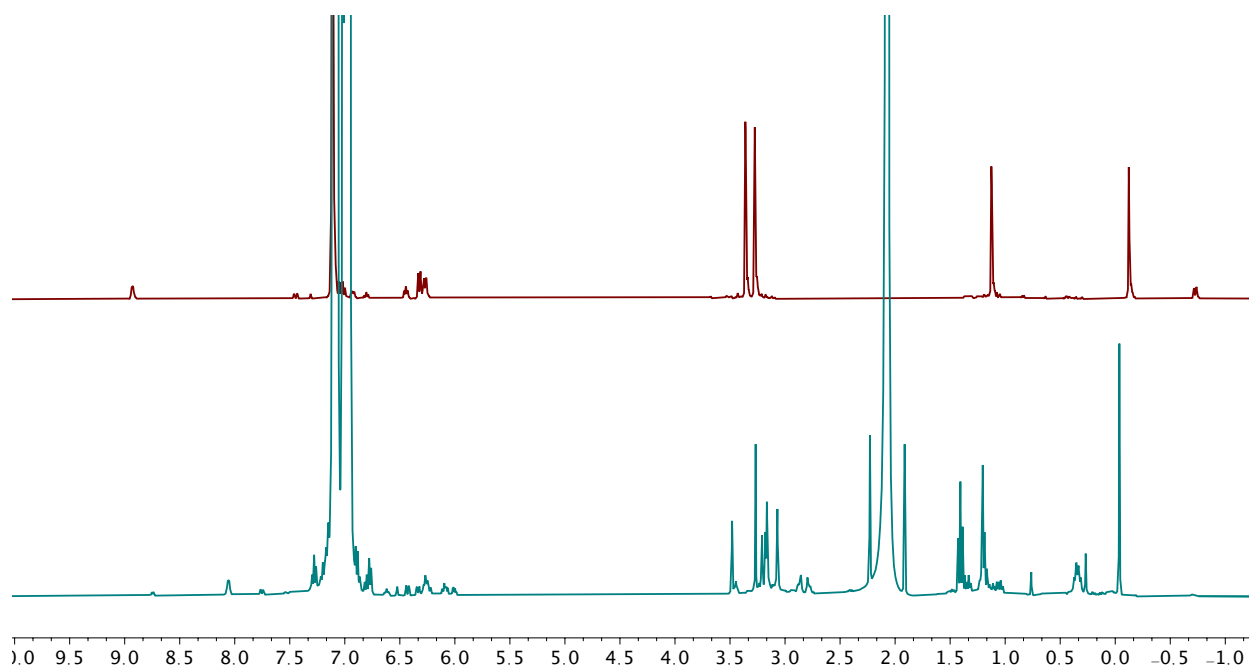


Figure S1: ^1H NMR spectra of: a) **1** (top) and b) **1** and 1 equiv. of AlEt_3 (bottom, AlEt_3 : 0.03M in toluene) in C_6D_6 .

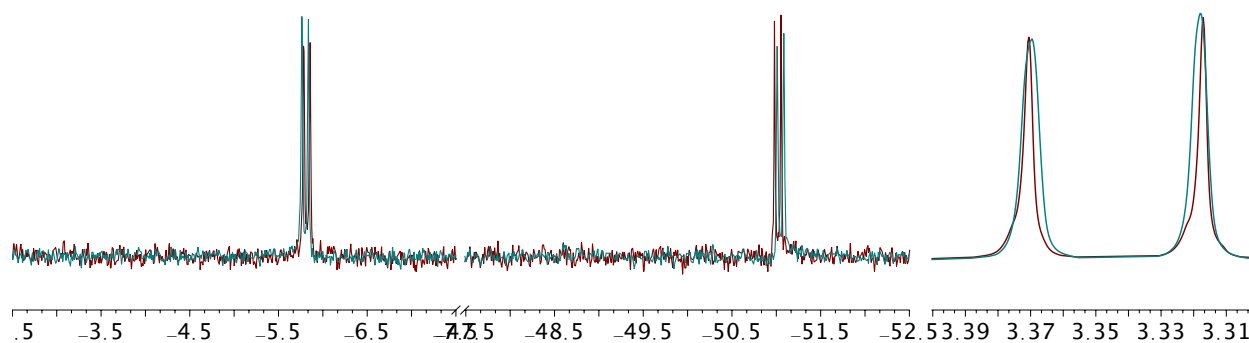


Figure S2: $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (left) and ^1H NMR spectra (right, only the resonances for methoxy groups) of **1** (red) and **1** + 1 equiv. of $\text{Al}(\text{O}^i\text{Pr})_3$ (green, condition: **1**: 5.8 mg, 0.0059 mmol; $\text{Al}(\text{O}^i\text{Pr})_3$: 1.2 mg, 0.0059 mmol; tol-d8: 0.5 mL; temperature: 70°C).

3 Synthesis of Ni/Zn Compounds

2/2^{Cl}: In the glove box, to a solution of **1** (29.6 mg, 0.03 mmol) in THF (5 mL) was added a suspension of 1 equiv. of ZnCl₂ (4.1 mg, 0.03 mmol) in THF (0.5 mL). The mixture was stirred for 30 min under room temperature, forming a red-orange solution. ¹H and ³¹P{¹H} NMR spectra of the reaction mixture indicate the generation of two new species (10% C₆D₆ was added for the ¹H NMR experiment). ³¹P{¹H} NMR (121 MHz, C₆D₆): δ -5.99 (d, ⁴J_{PP} = 12.1 Hz), -13.28 (d, ⁴J_{PP} = 12.1 Hz), -65.80 (d, ⁴J_{PP} = 12.1 Hz), -69.86 (d, ⁴J_{PP} = 12.1 Hz). Mixture of orange and red crystals were obtained via vapor diffusion of hexanes into THF solution of an *in-situ* mixture of **1** and 1 equiv. of ZnCl₂ and identified as **2** and **2^{Cl}**.

Independent synthesis of **2** (with a small amount of the other isomer, potentially **2^{Cl}**): In the glove box, to a solution of **1** (29.6 mg, 0.03 mmol) in THF (1.5 mL) was added a suspension of 0.9 equiv. of ZnCl₂ (3.7 mg, 0.027 mmol) in THF (0.5 mL). The mixture was stirred for 20 min under room temperature, forming a red-orange solution. To this solution was added just thawed pentane (18 mL), allowing the formation of a yellow suspension. Solids were collected via vacuum filtration, yielding **2** as orange powders (21.8 mg, 65%). ¹H NMR (400 MHz, C₆D₆): δ 8.84–8.82 (m, 2H, PyH), 7.62–7.59 (m, 1H, PhH), 7.49–7.47 (m, 1H, PhH), 7.48–7.45 (m, 1H, PhH), 7.24–7.20 (m, 1H, PhH), 7.06–7.04 (m, 4H, PhH), 6.96–6.94 (m, 1H, PyH), 6.65–6.63 (m, 2H, PyH), 6.39–6.37 (m, 4H, PhH), 6.26–6.24 (m, 4H, PhH), 3.57 (s, 12H, OCH₃), 3.47 (s, 12H, OCH₃), 1.10 (s, 9H, C(CH₃)₃), 0.26 (s, 9H, Si(CH₃)₃), -0.39–-0.42 (d, ³J_{HP} = 10.3 Hz, 2H, NiCH₂Si) (Note: resonances assigned to the other isomer: δ 6.20–6.19 (m, 4H, PhH), 6.12–6.10 (m, 4H, PhH), 3.33 (s, 12H, OCH₃), 3.28 (s, 12H, OCH₃), 1.15 (s, 9H, C(CH₃)₃), 0.36 (s, 9H, Si(CH₃)₃); Other resonances correspond to this isomer are overlapped with resonances of the major isomer). ¹³C{¹H} NMR (101 MHz, C₆D₆): 163.48 (broad s, 4C, Ar-C), 161.73 (broad s, 4C, Ar-C), 152.03

(m, 4C, Ar-C), 136.65 (m, 1C, Ar-C), 131.85 (m, 6C, Ar-C), 131.15 (s, 4C, Ar-C), 124.57 (s, 2C, Ar-C), 104.38 (m, 10C, Ar-C), 56.07 (s, 4C, OCH₃), 55.51 (s, 4C, OCH₃), 34.06 (s, 1C, C(CH₃)₃), 31.94 (s, 9C, C(CH₃)₃), 2.09 (s, 9C, SiMe₃), -14.58 (d, ²J_{CP} = 30.5 Hz, 1C, NiCH₂Si) (Note: resonances assigned to the other isomer: δ 161.58 (broad s, 4C, Ar-C), 137.92 (m, 1C, Ar-C), 108.85-108.14 (m, Ar-C), 56.00 (s, 4C, OCH₃), 55.16 (s, 4C, OCH₃), 34.21 (s, 1C, C(CH₃)₃), 32.03 (s, 9C, C(CH₃)₃), 2.98 (s, 9C, SiMe₃). Other resonances corresponded to this isomer are overlapped with resonances of the major isomer); ³¹P{¹H} NMR (121 MHz, C₆D₆): δ -5.62 (d, ⁴J_{PP} = 10.1 Hz, 1P), -62.37 (d, ⁴J_{PP} = 10.1 Hz, 1P). Anal. Calcd(%) for C₅₁H₆₃Cl₂NNiO₉P₂Si: C: 54.74, H: 5.67, N: 1.25; found: C: 55.72, H: 6.03, N: 1.86.

2^{Cl+} was obtained as red crystals via vapor diffusion of hexanes into THF solution of an *in-situ* mixture of **1** and 2 equiv. of ZnCl₂, or an *in-situ* mixture of **2/2^{Cl}** and 2 equiv. of ZnCl₂, in the presence of excess (2~5 equiv.) of pyridine. The resulting red crystals are poorly soluble in THF.

3: In the glove box, to a solution of **1** (29.6 mg, 0.03 mmol) in THF (1.5 mL) was added a suspension of 1 equiv. of ZnBr₂ (6.8 mg, 0.03 mmol) in THF (1.0 mL). The mixture was stirred for 30 min under room temperature, forming a red-orange solution. ³¹P{¹H} NMR spectrum of this reaction mixture indicate the generation of two new species assigned to **3** and possibly the bromide bridged analogue of **2^{Cl}**. ³¹P{¹H} NMR (121 MHz, C₆D₆): δ -5.78 (d, ⁴J_{PP} = 12.4 Hz), -9.62 (d, ⁴J_{PP} = 12.4 Hz), -63.42 (d, ⁴J_{PP} = 12.4 Hz), -66.33 (broad d). To prepare **3** in high purity (>95%), a solution of **1** (29.6 mg, 0.03 mmol) in THF (2 mL) was mixed with 0.8 equiv. of ZnBr₂ (5.4 mg, 0.024 mmol) in THF (2 mL). The mixture was stirred for 30 min under room temperature. After removal of volatiles, unreacted **1** was washed away by diethyl ether and desired products were collected via vacuum filtration (31.1 mg, 74%). ¹H NMR (400 MHz, C₆D₆): δ 8.79-8.77 (m, 2H, PyH), 7.66-7.62 (dd, ³J_{HP} = 10.8 Hz, ⁴J_{HH} = 2.5 Hz, 1H, PhH), 7.52-7.49 (dd, ³J_{HP} = 9.3 Hz, ⁴J_{HH}

= 2.5 Hz, 1H, PhH), 7.12–7.11 (m, 1H, PyH), 7.04–7.00 (m, 4H, PhH), 6.63–6.60 (m, 2H, PyH), 6.39–6.36 (dd, $^3J_{\text{HH}} = 8.3$ Hz, $^4J_{\text{HH}} = 3.6$ Hz, 4H, PhH), 6.29–6.26 (dd, $^3J_{\text{HH}} = 8.3$ Hz, $^4J_{\text{HH}} = 3.6$ Hz, 4H, PhH), 3.58 (s, 12H, OCH₃), 3.49 (s, 12H, OCH₃), 1.13 (s, 9H, C(CH₃)₃), 0.26 (s, 9H, Si(CH₃)₃), -0.40–-0.43 (d, $^3J_{\text{HP}} = 10.1$ Hz, 2H, NiCH₂Si); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C₆D₆): 163.45 (s, 2C, Ar-C), 163.42 (s, 2C, Ar-C), 161.72 (s, 4C, Ar-C), 152.07 (m, 4C, Ar-C), 136.80 (m, 1C, Ar-C), 131.97 (m, 6C, Ar-C), 131.20 (s, 4C, Ar-C), 124.70 (s, 2C, Ar-C), 104.35 (m, 10C, Ar-C), 56.11 (s, 4C, OCH₃), 55.58 (s, 4C, OCH₃), 34.13 (s, 1C, C(CH₃)₃), 32.00 (s, 9C, C(CH₃)₃), 2.13 (s, 9C, SiMe₃), -14.26 (d, $^2J_{\text{CP}} = 30.5$ Hz, 1C, NiCH₂Si); $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C₆D₆): δ -5.80 (d, $^4J_{\text{PP}} = 10.3$ Hz, 1P), -63.39 (d, $^4J_{\text{PP}} = 10.3$ Hz, 1P). Anal. Calcd(%) for C₅₁H₆₃Br₂NNiO₉P₂Si: C: 50.71, H: 5.26, N: 1.16; found: C: 52.43, H: 5.18, N: 0.99.

NMR Spectra

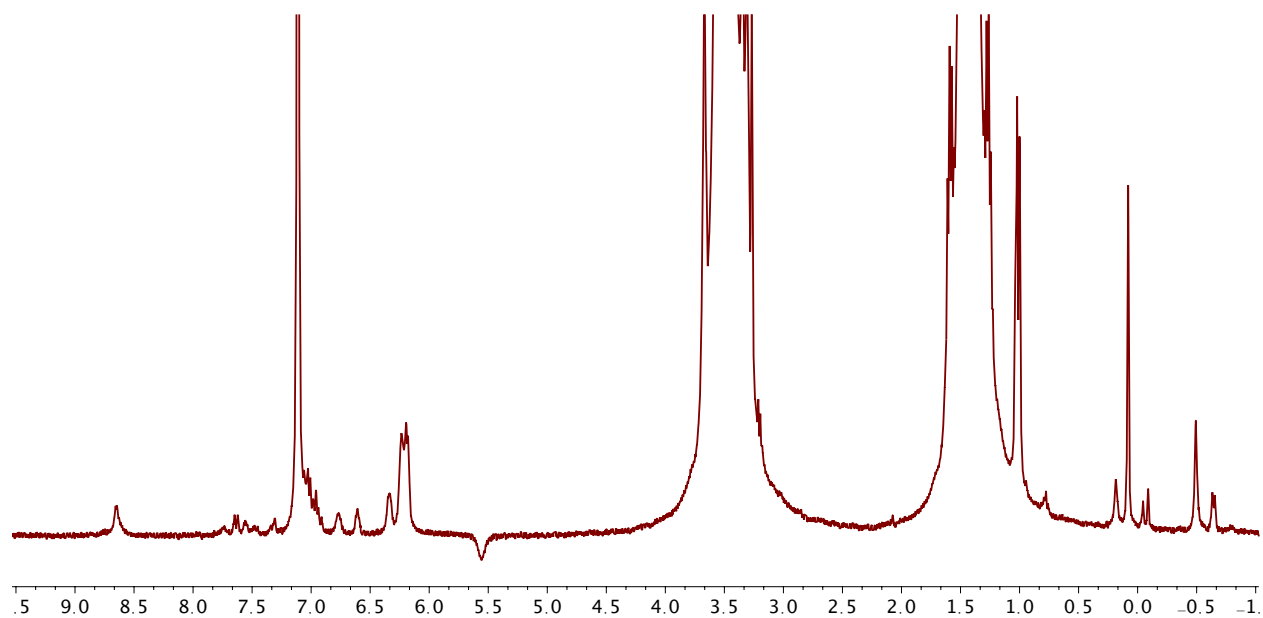


Figure S3: ^1H NMR spectrum of **1** + 1 equiv. of ZnCl_2 in 10% C_6D_6 /90% THF-H8.

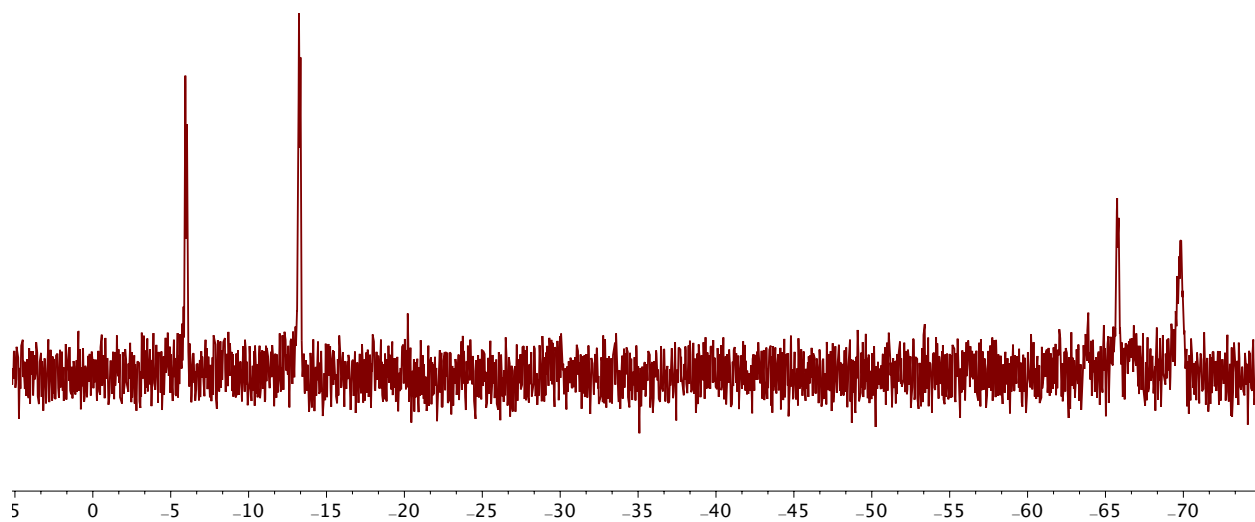


Figure S4: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of two isomers (crude mixture of **1** + 1 equiv. of ZnCl_2) in 10% C_6D_6 /90% THF-H8.

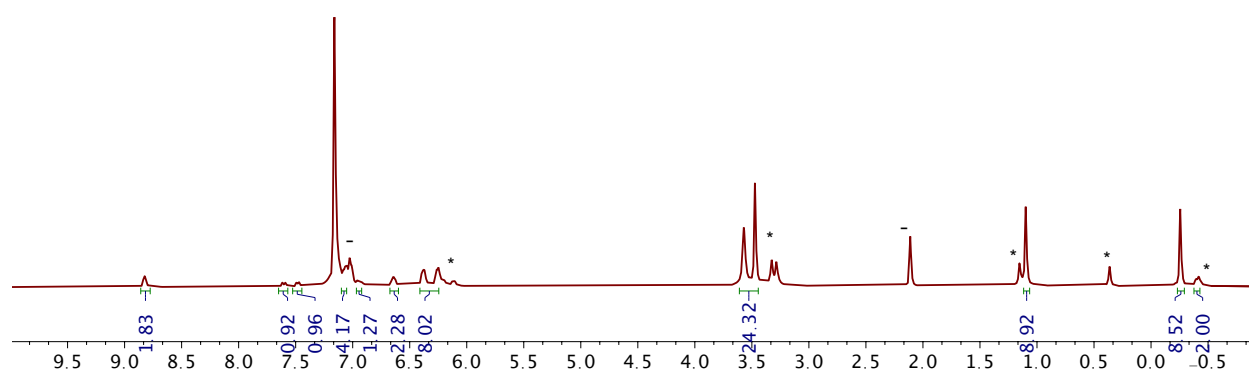


Figure S5: ^1H NMR spectrum of **2** in C_6D_6 (*: the other isomer, -: toluene, only resonances of **2** is integrated).

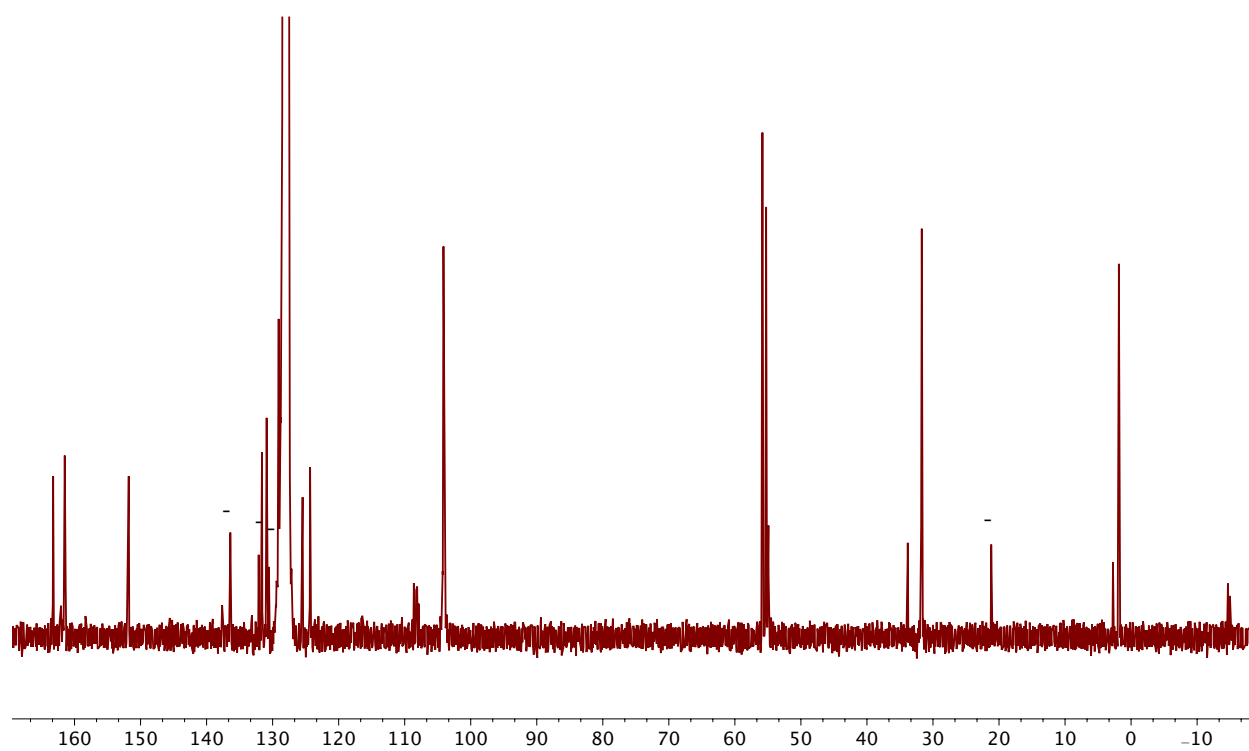


Figure S6: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** in C_6D_6 (-: toluene).

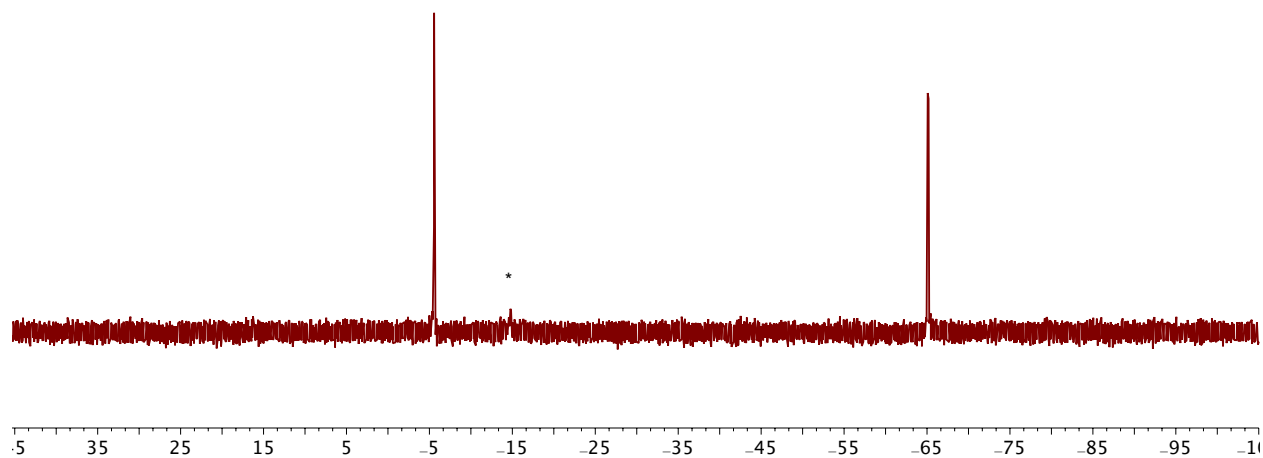


Figure S7: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** in C_6D_6 (*: the other isomer).

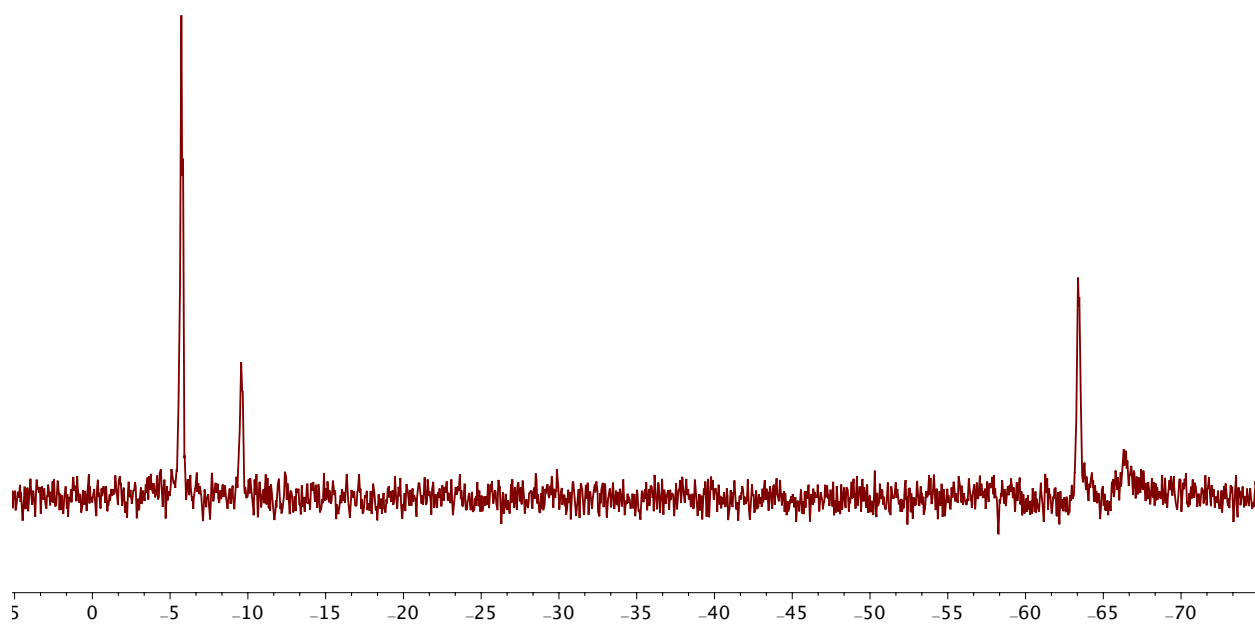


Figure S8: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of two isomers (crude mixture of **1** + 1 equiv. of ZnBr_2) in THF-H8.

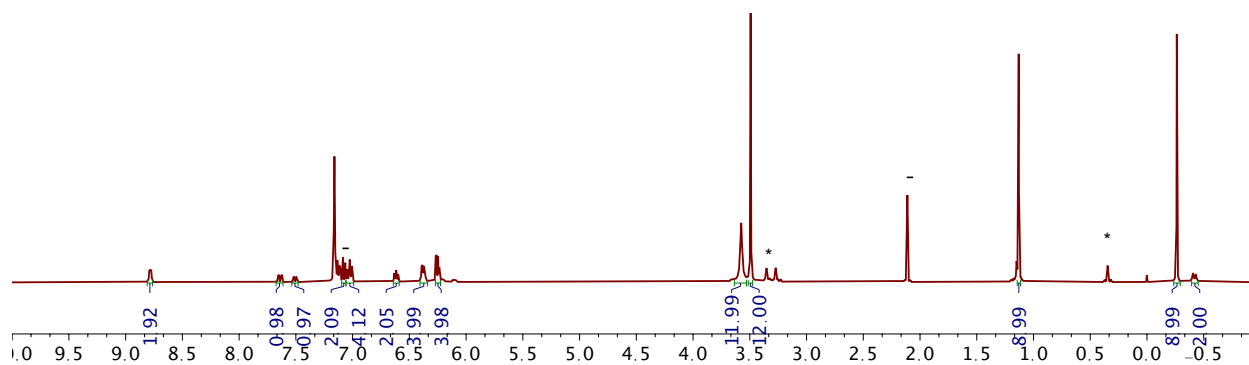


Figure S9: ^1H NMR spectrum of **3** in C_6D_6 (*: the other isomer, -: toluene, only resonances of **3** is integrated).

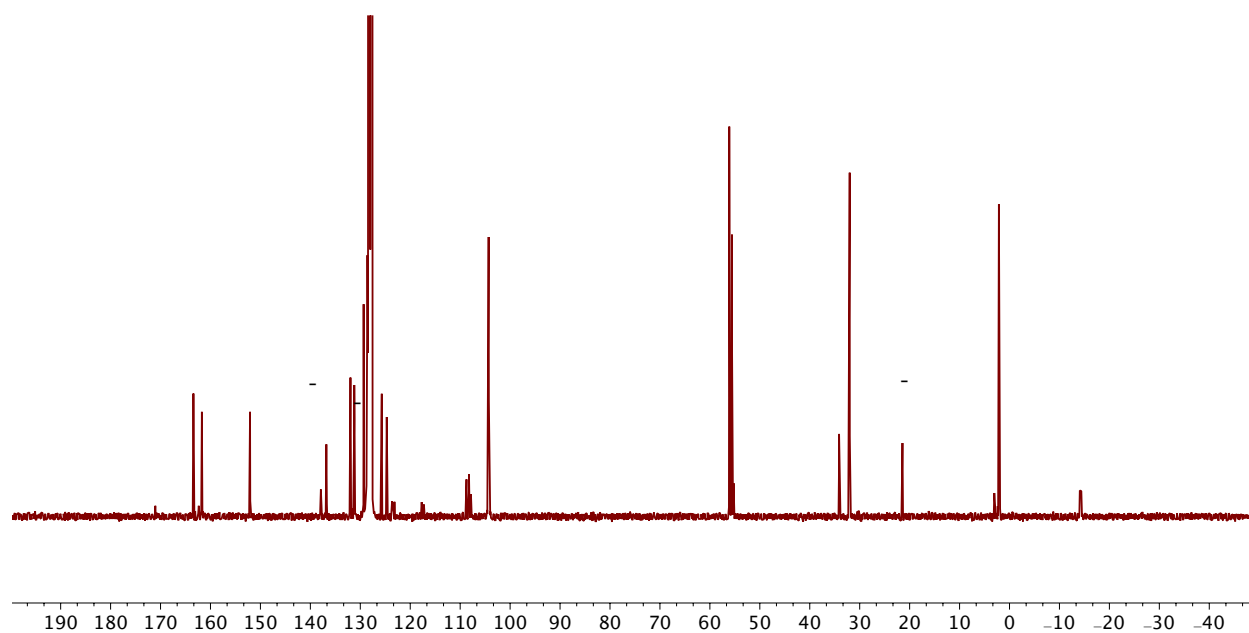


Figure S10: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** in C_6D_6 (-: toluene).

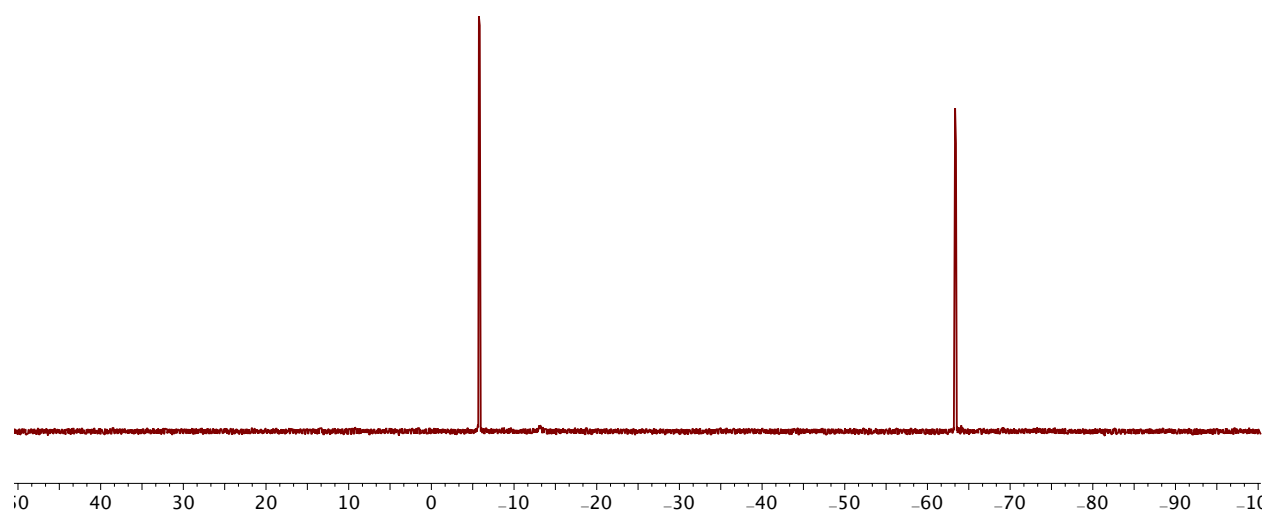


Figure S11: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** in C_6D_6 .

4 Supplemental Data for Ethylene Polymerization and Ethylene/tBA Copolymerization

4.1 General procedure for Fisher-Porter type reactor runs for preparation of polyethylene.

This high-pressure setup consists of a 3 oz Andrews glass pressure reaction vessel equipped with Swagelok valves and a gauge. For all ethylene homopolymerization, this setup was brought into the glove box with a magnetic stir bar and charged with a toluene mixture (5 mL) of the desired amounts of the nickel complex and the secondary metal additive (if applicable). The setup was brought out of the box and clamped firmly over a hot plate which was preheated to desired temperature. The solution was stirred vigorously (1200 rpm). A nylon core hose equipped with quick connect adaptors was purged with ethylene for 1 minute and the pressure was set to 15 psi. The hose was connected to the setup and the setup was filled with ethylene. The pressure was increased to 100 psi. After the desired time (15 min), the ethylene hose was disconnected, the setup was vented and the reaction mixture was quenched with acidified methanol (3 times the reaction volume, 15 mL) to precipitate the polymer, which was collected as a white solid by filtration over a fine frit. All of the precipitates were dried under vacuum over at least 24 hours before the polymer masses were recorded.

4.2 Ethylene homopolymerization results.

Table S1 Ethylene homopolymerization results

Entry ^a	Catalyst + n (equiv.) additive	Yield (g)	Act.(kg/(mol·h))
1	1	0.682	682
2	1	0.747	747
3	1 + 5 ZnCl ₂	0.052	52
4	1 + 5 ZnCl ₂	0.017	17
5	2/2 ^{Cl}	<0.01	<10
6	2/2 ^{Cl}	<0.01	<10
7	2 ^{Cl+}	<0.01	<10
8	2 ^{Cl+}	<0.01	<10
9	1 + 5 ZnBr ₂	<0.01	<10
10	1 + 5 ZnBr ₂	<0.01	<10
11	3	<0.01	<10
12	3	<0.01	<10
13	1 + 5 Al(O ⁱ Pr) ₃	1.322	1322
14	1 + 5 Al(O ⁱ Pr) ₃	0.91	910
15	1 + 5 AlEt ₃	<0.01	<10
16	1 + 5 AlEt ₃	<0.01	<10

^aUnless specified, V(total) = 5 mL, [Ni] = 4 μmol, pressure = 100 psi, T = 70 °C, toluene solvent, time = 15 min. ^bAct.= (kg/(mol·h)).

4.3 General procedure for high throughput parallel polymerization reactor (PPR) runs for preparation of ethylene/tBA copolymers.

Polyolefin catalysis screening was performed in a high throughput parallel polymerization reactor (PPR) system. The PPR system was comprised of an array of 48 single cell (6 x 8 matrix) reactors in an inert atmosphere glovebox. Each cell was equipped with a glass insert with an internal working liquid volume of approximately 5 mL. Each cell had independent controls for pressure and was continuously stirred at 800 rpm. Catalysts and secondary metal additives, unless otherwise noted, were prepared in toluene. All liquids (i.e., solvent, tBA, and catalyst solutions) were added via robotic syringes. Gaseous reagents (i.e., ethylene) were added via a gas injection port. Prior to each run, the reactors were heated to 50 °C, purged with ethylene, and vented.

All desired cells were injected with tBA followed with a portion of toluene. The reactors were heated to the run temperature and then pressured to the appropriate psig with ethylene. Catalysts (with additives) were then added to the cells. Each catalyst addition was chased with a small amount of toluene so that after the final addition, a total reaction volume of 5 mL was reached. Upon addition of the catalyst, the PPR software began monitoring the pressure of each cell. The desired pressure (within approximately 2-6 psig) was maintained by the supplemental addition of ethylene gas by opening the valve at the set point minus 1 psi and closing it when the pressure reached 2 psi higher. All drops in pressure were cumulatively recorded as “Uptake” or “Conversion” of the ethylene for the duration of the run or until the uptake or conversion requested value was reached, whichever occurred first. Each reaction was then quenched by addition of 1% oxygen in nitrogen for 30 seconds at 40 psi higher than the reactor pressure. The shorter the “Quench Time”, the more active the catalyst. In order

to prevent the formation of too much polymer in any given cell, the reaction was quenched upon reaching a predetermined uptake level of 80 psig. After all the reactors were quenched they were allowed to cool to about 60 °C. They were then vented and the tubes were removed. The polymer samples were then dried in a centrifugal evaporator at 60 °C for 12 hours, weighed to determine polymer yield and submitted for IR (tBA incorporation) and GPC (molecular weight) analysis.

4.4 Procedure for characterization of ethylene/tBA copolymers.

Gel permeation chromatography (GPC).

High temperature GPC analysis was performed using a Dow Robot Assisted Delivery (RAD) system equipped with a Polymer Char infrared detector (IR5) and Agilent PLgel Mixed A columns. Decane (10 µL) was added to each sample for use as an internal flow marker. Samples were first diluted in 1,2,4-trichlorobenzene (TCB) stabilized with 300 ppm butylated hydroxyl toluene (BHT) at a concentration of 10 mg/mL and dissolved by stirring at 160°C for 120 minutes. Prior to injection the samples are further diluted with TCB stabilized with BHT to a concentration of 3 mg/mL. Samples (250 µL) are eluted through one PL-gel 20 µm (50 x 7.5 mm) guard column followed by two PL-gel 20 µm (300 x 7.5 mm) Mixed-A columns maintained at 160 °C with TCB stabilized with BHT at a flowrate of 1.0 mL/min. The total run time was 24 minutes. To calibrate for molecular weight (MW) Agilent EasiCal polystyrene standards (PS-1 and PS-2) were diluted with 1.5 mL TCB stabilized with BHT and dissolved by stirring at 160 °C for 15 minutes. These standards are analyzed to create a 3rd order MW calibration curve. Molecular weight units are converted from polystyrene (PS) to polyethylene (PE) using a daily Q-factor calculated to be around 0.4 using the average of 5 Dowlex 2045 reference samples.

Fourier-transform infrared spectroscopy (FTIR).

The 10 mg/mL samples prepared for GPC analysis are also utilized to quantify tert-butyl acrylate (tBA) incorporation by Fourier Transform infrared spectroscopy (FTIR). A Dow robotic preparation station heated and stirred the samples at 160°C for 60 minutes then deposited 130 μ L portions into stainless wells promoted on a silicon wafer. The TCB was evaporated off at 160°C under nitrogen purge. IR spectra were collected using a Nexus 6700 FT-IR equipped with a DTGS KBr detector from 4000-400 cm^{-1} utilizing 128 scans with a resolution of 4. Ratio of tBA (C=O: 1762-1704 cm^{-1}) to ethylene (CH₂: 736-709 cm^{-1}) peak areas were calculated and fit to a linear calibration curve to determine total tBA.

Differential scanning calorimetry (DSC).

Differential scanning calorimetry analyses was performed on solid polymer samples using a TA Instruments, Inc. Discovery Series or TA Instruments, Inc., DSC2500, programmed with the following method: Equilibrate at 175.00 °C; Isothermal for 3 minutes; Ramp 30.00 °C/min to 0.00 °C; Ramp 10.00 °C/min to 175.00 °C; Data was analyzed using TA Trios software.

4.5 Original data of ethylene/tBA copolymerization trials.

Table S2. Ethylene/tBA copolymerization by in-situ mixture of **1** and aluminum additives (Original data for Table 1)

Entry ^a	Catalyst + n (equiv.) additive	[tBA]/[1]	t (s)	Yield (mg)	Act. ^b	Mw*10 ⁻³	PDI	%Mol t- BA	Tm (°C)
1 ^c	1	1000	2250	103	659	53.08	2.2	2.24	110
2 ^c	1	1000	3601	118	472	53.98	2.2	1.99	111
3 ^c	1	1000	3447	123	514	55.79	2.2	2.01	111
4 ^c	1 + 1 Al(O ⁱ Pr) ₃	1000	1857	123	954	53.30	2.3	2.16	111
5 ^c	1 + 1 Al(O ⁱ Pr) ₃	1000	1600	109	981	49.43	2.2	2.22	110
6 ^c	1 + 1 Al(O ⁱ Pr) ₃	1000	1653	106	923	50.63	2.4	2.21	111
7 ^c	1 + 2 Al(O ⁱ Pr) ₃	1000	1666	113	977	52.21	2.2	2.15	110
8 ^c	1 + 2 Al(O ⁱ Pr) ₃	1000	1480	103	1002	52.23	2.3	2.11	111
9 ^c	1 + 2 Al(O ⁱ Pr) ₃	1000	1582	114	1037	50.32	2.2	2.14	110
10 ^c	1 + 5 Al(O ⁱ Pr) ₃	1000	1569	109	1000	50.05	2.3	2.16	110
11 ^c	1 + 5 Al(O ⁱ Pr) ₃	1000	1590	112	1015	52.10	2.4	2.09	110
12 ^c	1 + 5 Al(O ⁱ Pr) ₃	1000	1628	114	1008	51.42	2.4	2.32	110
13	1 + 1 Al(OEt)Et ₂	1000	3601	119	476	58.20	2.4	2.15	111
14 ^c	1 + 1 Al(OEt)Et ₂	1000	3369	117	500	54.57	2.2	2.06	111
15 ^c	1 + 1 Al(OEt)Et ₂	1000	3523	112	458	55.38	2.5	2.07	111
16	1 + 2 Al(OEt)Et ₂	1000	3601	81	324	52.64	2.2	2.27	110
17	1 + 2 Al(OEt)Et ₂	1000	3602	68	272	53.64	2.2	2.12	111
18	1 + 2 Al(OEt)Et ₂	1000	3601	63	252	51.56	2.3	2.27	110
19	1 + 5 Al(OEt)Et ₂	1000	3600	27	108	45.07	2.2	2.42	109
20	1 + 5 Al(OEt)Et ₂	1000	3601	25	100	47.13	2.2	2.27	110
21	1 + 5 Al(OEt)Et ₂	1000	3600	21	84	48.81	2.6	2.31	109
22	1 + 1 AlEt ₃	1000	3601	<2	<10	N.D.	N.D.	N.D.	N.D.
23	1 + 1 AlEt ₃	1000	3601	<2	<10	N.D.	N.D.	N.D.	N.D.
24	1 + 1 AlEt ₃	1000	3601	<2	<10	N.D.	N.D.	N.D.	N.D.
25	1	2000	3600	70	280	34.59	2.3	4.54	99
26	1	2000	3601	67	268	35.04	2.4	5.01	94
27	1 + 1 Al(O ⁱ Pr) ₃	2000	3309	118	514	41.30	2.4	4.42	99
28	1 + 1 Al(O ⁱ Pr) ₃	2000	3494	125	515	38.24	2.3	4.69	100

^aUnless specified, V(total) = 5 mL, [Ni] = 0.25 μmol, ethylene pressure = 400 psi, T = 90 °C, toluene solvent, time = 1 h. ^bAct. = (kg/(mol·h)). ^cPolymerization runs were stopped when ethylene uptake reached 80.13 psi (<1 h).

5 Crystallographic Information

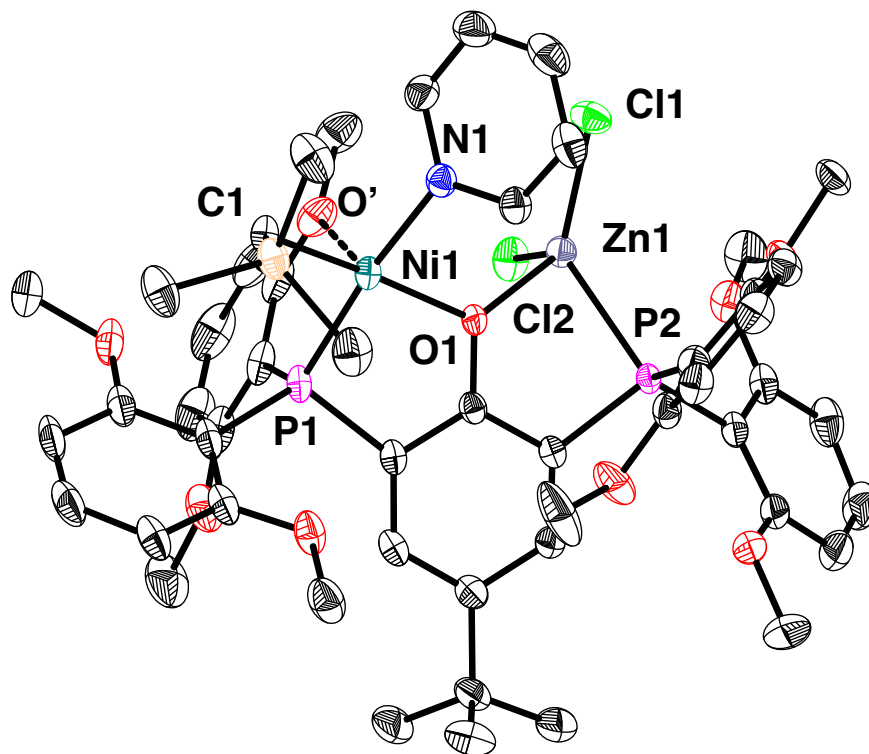


Figure S12 Solid-state structure of **2**. Ellipsoids are shown at the 50% probability level. Hydrogen atoms and solvent molecules excluded for clarity.

Special Refinement Details for 2: Complex **2** crystallizes in a $P_{21/c}$ space group with the full molecule, half of a benzene molecule and two THF molecules in the asymmetric unit. A disordered THF molecule is observed and is refined isotropically to prevent NPDs.

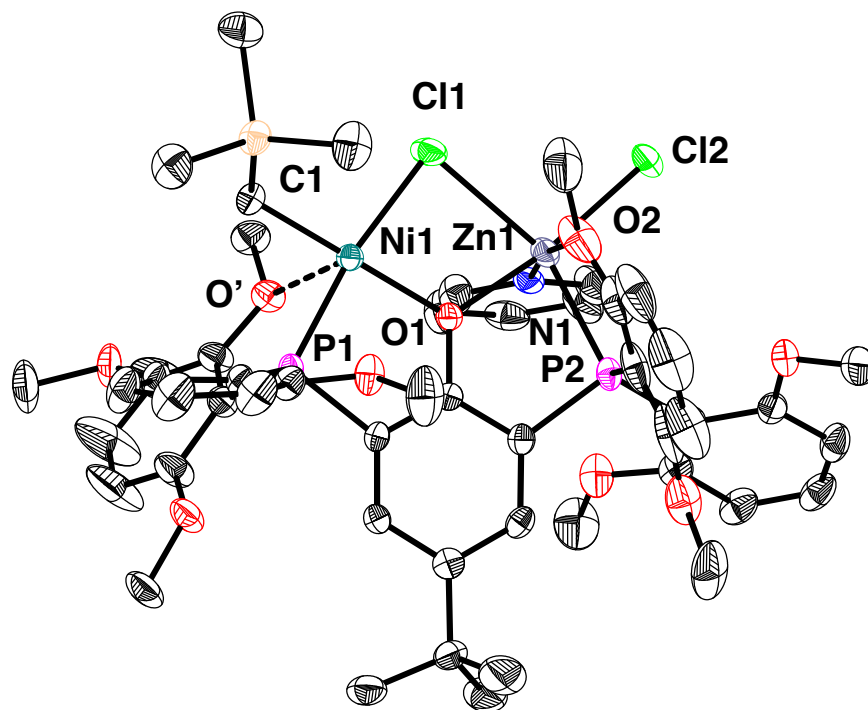


Figure S13 Solid-state structure of **2^{Cl}**. Ellipsoids are shown at the 50% probability level. Hydrogen atoms and solvent molecules excluded for clarity. Disordered dimethoxyphenyl and chlorides excluded for clarity.

Special Refinement Details for 2^{Cl}: Complex **2^{Cl}** crystallizes in a $P_{21/n}$ space group with the full molecule and one benzene molecule in the asymmetric unit. Two chlorides (Cl1 and Cl2) are modelled with two-site disorder with occupancies of 0.746 and 0.254. One of the dimethoxyphenyl groups is also modelled with two-site disorder with occupancies of 0.746 and 0.254.

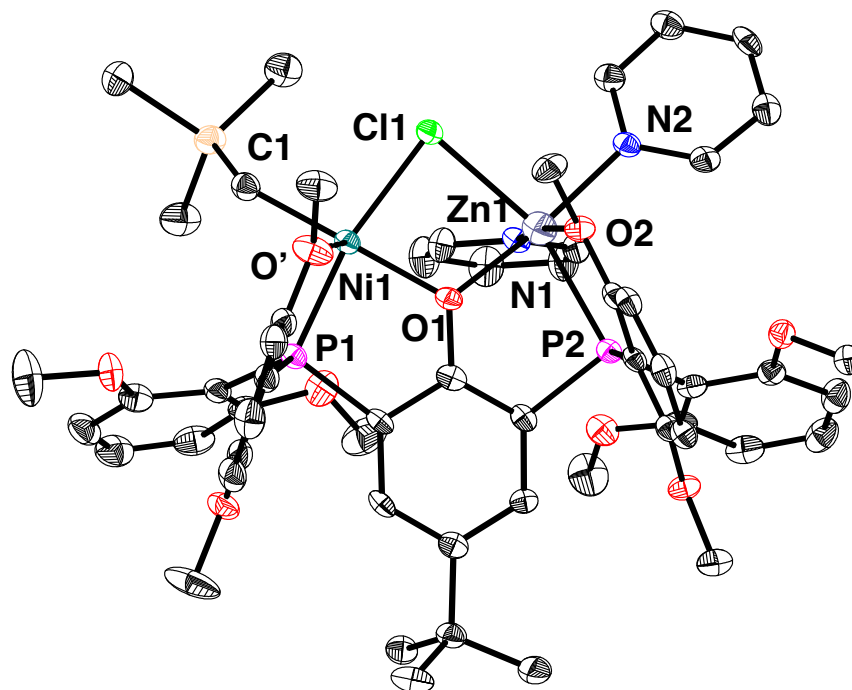


Figure S14 Solid-state structure of $2^{\text{Cl}+}$. Ellipsoids are shown at the 50% probability level. Hydrogen atoms, solvent molecules, and the counterion are excluded for clarity.

Special Refinement Details for $2^{\text{Cl}+}$: Complex $2^{\text{Cl}+}$ crystallizes in a P-1 space group with the full molecule and one benzene molecule in the asymmetric unit.

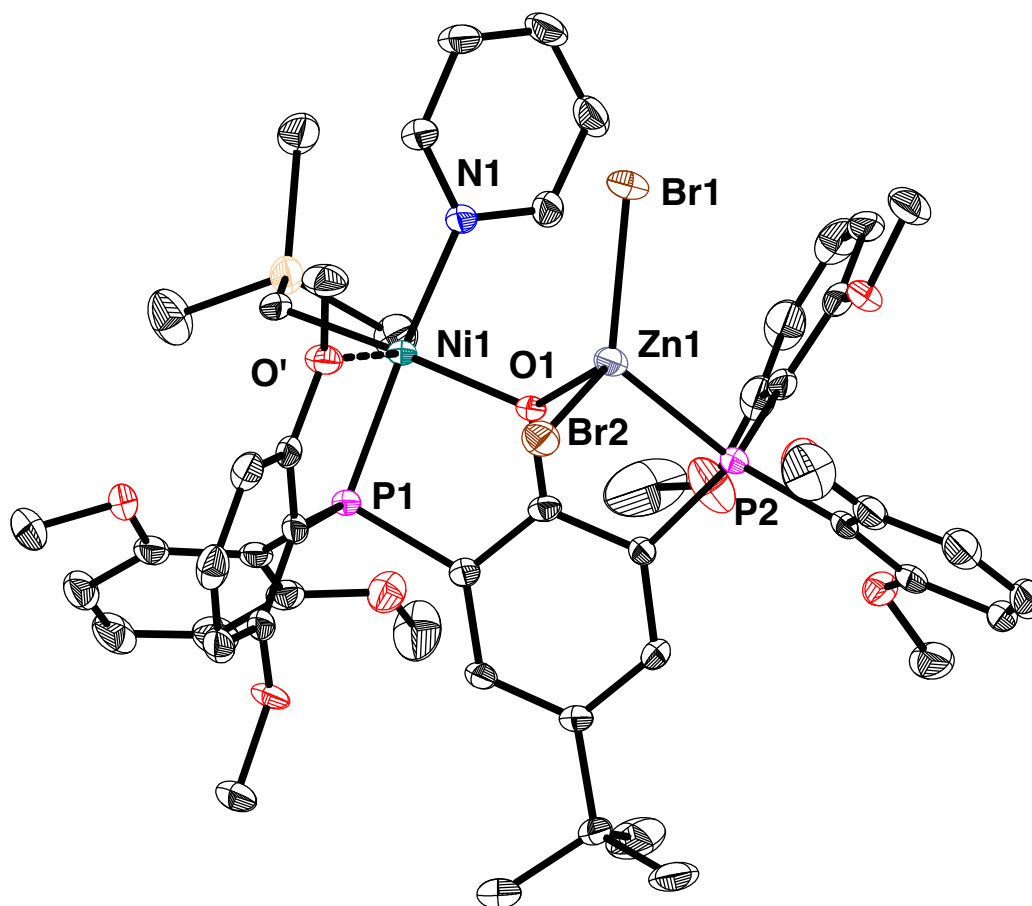


Figure S15 Solid-state structure of **3**. Ellipsoids are shown at the 50% probability level. Hydrogen atoms and solvent molecules excluded for clarity.

Special Refinement Details for 2 Complex **3** crystallizes in a P-1 space group with the full molecule and one diethylether molecule in the asymmetric unit.

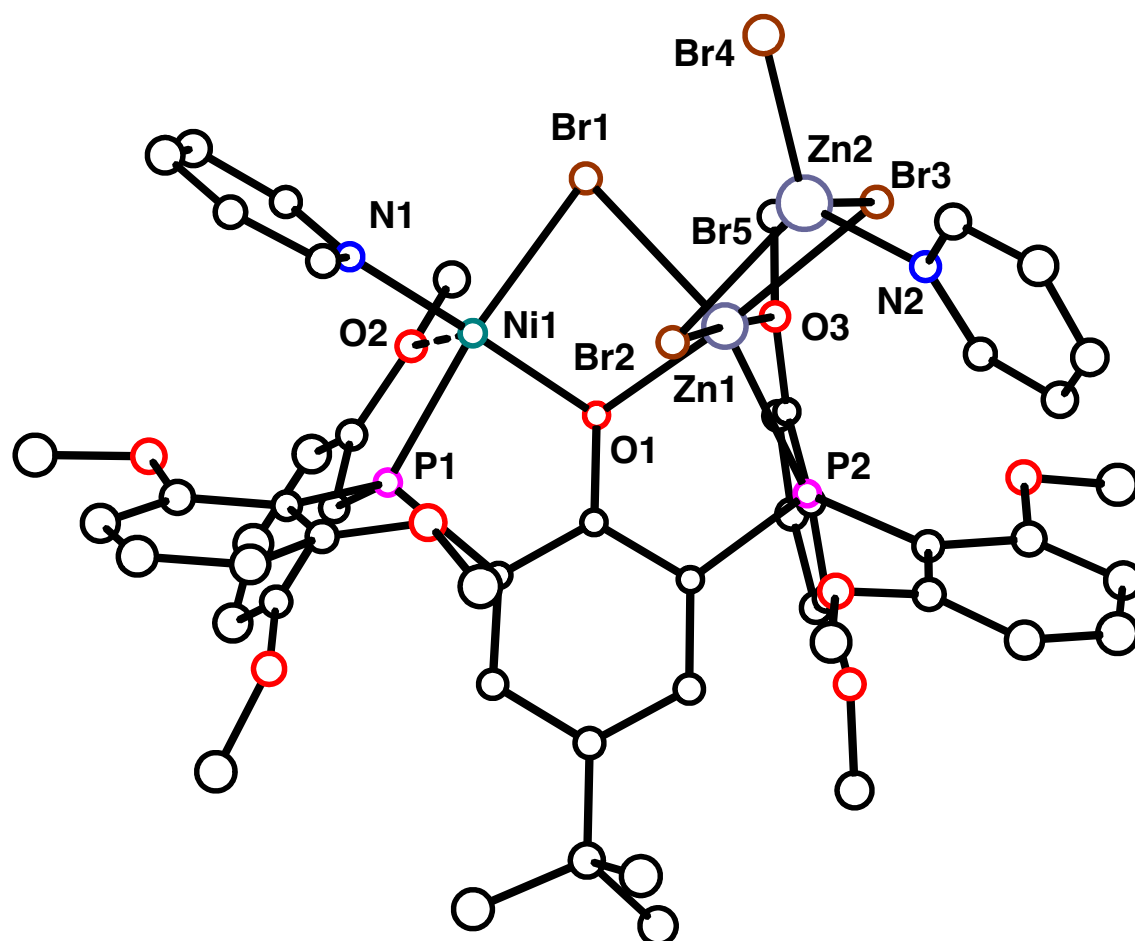


Figure S16. Solid-state structure of a bromide bridged Ni/Zn complex. Data quality is only sufficient for depicting the connectivity. Hydrogen atoms and solvent molecules excluded for clarity.

Table S3: Crystal and refinement data (part 1)

	2	2^{Cl}
Empirical formula	C _{61.42} H _{79.99} Cl ₂ NNiO _{10.86} P ₂ SiZn	C ₅₇ H ₆₉ Cl ₂ NNiO ₉ P ₂ SiZn
Formula weight	1290.98	1194.14
Temperature/K	100 K	100 K
Crystal system	Monoclinic	Monoclinic
Space group	P _{21/C}	P _{21/n}
a/Å	13.826(2)	12.897(3)
b/Å	17.674(2)	19.086(7)
c/Å	26.488(3)	23.021(6)
α/°	90	90
β/°	91.636(11)	90.746(16)
γ/°	90	90
Volume/Å ³	6470.2(15)	5666(3)
Z	4	4
ρ _{calc} /cm ³	1.325	1.403
μ/mm ⁻¹	2.677	2.989
F(000)	2713	2504
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
Reflections collected	136826	51336
Independent reflections	13826	11686
Goodness-of-fit on F ²	1.039	0.934
Final R indexes [I ≥ 2σ (I)]	R ₁ = 5.66 % R ₂ = 15.73 %	R ₁ = 6.40 % R ₂ = 17.76 %

Table S4: Crystal and refinement data (part 2)

	2^{Cl+}	3
Empirical formula	C _{33.5} H _{39.5} Cl _{1.5} N _{1.5} Ni _{0.5} O _{4.50} PSi _{0.50} Zn	C ₅₅ H ₇₃ Br ₂ NNiO ₁₀ P ₂ SiZn
Formula weight	745.80	1282.07
Temperature/K	100 K	100 K
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a/Å	11.564(4)	12.358(13)
b/Å	13.159(3)	14.836(6)
c/Å	24.094(6)	17.474(11)
α/°	82.753(18)	93.63(2)
β/°	82.18(2)	99.68(3)
γ/°	74.389(16)	110.98(3)
Volume/Å ³	3482.9(16)	2922(4)
Z	4	4
ρ _{calc} /cm ³	1.422	1.457
μ/mm ⁻¹	3.581	3.668
F(000)	1548	1324
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
Reflections collected	58754	92640
Independent reflections	13466	12436
Goodness-of-fit on F ²	1.084	1.495
Final R indexes [I ≥ 2σ (I)]	R ₁ = 6.38 % R ₂ = 13.99 %	R ₁ = 3.83 % R ₂ = 16.15 %

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