Supporting Information for:

Investigations into Asymmetric Post-Metallocene Group 4 Complexes for the Synthesis of Highly Regioirregular Polypropylene

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Experimental Section

General Considerations and Instrumentation

All air- and moisture-sensitive compounds were manipulated using standard high-vacuum and Schlenk techniques or manipulated in a glovebox under a nitrogen atmosphere. Solvents for air- and moisture-sensitive reactions were dried over sodium benzophenone ketyl and stored over titanocene where compatible, or dried by the method of Grubbs.[1] $TiCl_2(NMe)_2$[2], $ZrBn_4$, $HfBn_4$[3], (NNO)$TiCl_2$ (**4**)[4], *N*-benzyl-2-bromoaniline[5], *N*-Adamant-1-yl-2-bromoaniline[6], and 2-bromo-6-(3,5-di-t-butyl-2-(methoxymethoxy)phenyl)pyridine[4] were prepared following literature procedures. 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was purchased from Sigma Aldrich and distilled prior to use. Butyllithium solution, potassium phosphate tribasic, barium hydroxide octahydrate and palladium(II)acetate were purchased from Sigma Aldrich and used as received. $Pd(PPh_3)_4$ and 2-(dicyclohexylphosphino)biphenyl were purchased from Strem and used as received. Pinacolborane was purchased from Alfa Aesar. 1,4-dioxane and pinacolborane were dried over 3 Å molecular sieves prior to use. Methylaluminoxane (MAO) was purchased as a toluene solution from Albemarle and was dried in vacuo at 150 °C overnight to remove free trimethylaluminum before use. Propylene was dried by passage through a column of activated alumina and molecular sieves. Benzene-d_6, toluene-d_8, C_6D_5Cl, $CDCl_3$ and 1,1,2,2-tetrachloroethane-d_2 (TCE-d_2) were purchased from Cambridge Isotopes. Benzene-d_6 and toluene-d_8 were dried over sodium benzophenone ketyl then over titanocene. C_6D_5Cl was distilled from CaH_2 and passed through a plug of activated alumina prior to use. NMR spectra were recorded on Varian Mercury 300, Varian INOVA 500 or Varian INOVA 600

spectrometers and referenced to the solvent residual peak. High resolution mass spectra (HRMS) were obtained at the California Institute of Technology Mass Spectral Facility using a JEOL JMS-600H magnetic sector mass spectrometer. Elemental analyses were performed by Midwest Microlab LLC, Indianapolis, IN 46250 or Robertson Microlit Laboratories, Inc., Ledgewood, NJ 07852. X-ray quality crystals were grown as indicated in the experimental procedures for each complex. The crystals were mounted on a glass fiber with Paratone-N oil. Data collection was carried out on a Bruker KAPPA APEX II diffractometer with a 0.71073 Å MoKα source. Structures were determined using direct methods with standard Fourier techniques using the Bruker AXS software package. In some cases, Patterson maps were used in place of the direct methods procedure. Some details regarding crystal data and structure refinement are available in Tables 1. Selected bond lengths and angles are supplied in the corresponding figures of the manuscript.

L2-MOM (^{Bn}NNO-MOM). Followed the previously reported procedure for **L1-MOM** starting from *N*-benzyl-2-bromoaniline.[4] Crude yield: 91% yellow oil; some impurities were subsequently removed following deprotection. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33 (s, 9H, C(C*H*$_3$)$_3$), 1.50 (s, 9H, C(C*H*$_3$)$_3$), 3.23 (s, 3H, CH_2OCH_3), 4.49 (s, 2H, CH_2OCH_3), 4.50 (d, *J* = 4.3 Hz, 2H, benzyl-C*H*$_2$), 6.69 (dd, *J* = 8.3, 1.2 Hz, 1H, aryl-C*H*), 6.76 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H, aryl-C*H*), 7.14 – 7.17 (m, 2H, aryl-C*H*), 7.20 – 7.24 (m, 1H, aryl-C*H*), 7.29 – 7.33 (m, 1H, aryl-C*H*), 7.42 (d, *J* = 2.5 Hz, 1H, aryl-C*H*), 7.47 (d, *J* = 2.6 Hz, 1H, aryl-C*H*), 7.54 (dd, *J* = 7.7, 0.9 Hz, 1H, aryl-C*H*), 7.69 – 7.74 (m, 2H, aryl-C*H*), 7.84 (t, *J* = 7.9 Hz, 1H, aryl-C*H*), 9.44 (s, 1H, N*H*). ^{13}C NMR (126 MHz, $CDCl_3$) δ 31.02

(C(*C*H$_3$)$_3$), 31.63 (C(*C*H$_3$)$_3$), 34.71 *C*(CH$_3$)$_3$, 35.58 *C*(CH$_3$)$_3$, 47.39 (benzyl-*C*H$_2$), 57.56 (CH$_2$O*C*H$_3$), 99.73 (*C*H$_2$OCH$_3$), 112.07, 112.94, 115.80, 119.92, 121.57, 124.86, 126.35, 126.62, 126.88, 128.41, 129.25, 130.50, 134.14, 137.27, 139.93, 142.45, 145.99, 148.16, 151.72, 156.54, 159.50 (aryl-*C*). HRMS (FAB+) *m*/*z*: calcd for $C_{34}H_{40}N_2O_2$ $[M + H]^+$ 508.3090; found 508.3081.

L2-H$_2$ (^{Bn}NNO-H$_2$) 1.0010 g of **L2-MOM** was placed in a 100 mL round bottom flask charged with a stirbar and 5 mL of THF and 2 mL of MeOH were added to give a yellow solution. The flask was cooled to 0 ℃ with a water-ice bath; a 6 mL solution of 1:1 MeOH/conc. HCl was added dropwise resulting in the solution turning brighter yellow. The reaction was stirred for 30 min at 0 ℃, then removed from the ice bath and allowed to reach room temperature while stirring was continued overnight. The solution was then quenched with 2 M aq. NaOH to give a solution with neutral pH. The organic layer was extracted with diethyl ether (3 × 70 mL) and the combined organics were dried over magnesium sulfate and rotovapped to reveal a yellow oil, which was redissolved in dichloromethane and passed through a SiO_2 plug to give an orange oil. Recrystallization by dissolving in hot hexanes followed by cooling in the freezer yielded bright yellow crystals. 412.7 mg (45% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.40 (s, 9H, C(C*H*$_3$)$_3$), 1.49 (s, 9H, C(C*H*$_3$)$_3$), 4.42 (s, 2H, benzyl-C*H*$_2$), 6.08 (s, 1H, N*H*), 6.70 (dd, *J* = 8.3, 1.0 Hz, 1H, aryl-C*H*), 6.80 (td, *J* = 7.4, 1.1 Hz, 1H, aryl-C*H*), 7.18 – 7.32 (m, 4H, aryl-C*H*), 7.40 (dd, *J* = 7.6, 1.6 Hz, 1H, aryl-C*H*), 7.42 – 7.46 (m, 3H, aryl-C*H*), 7.48 (dd, *J* = 7.7, 0.9 Hz, 1H, aryl-C*H*), 7.69 (d, *J* = 2.4 Hz, 1H, aryl-C*H*), 7.85 (d, *J* = 7.7 Hz, 1H, aryl-C*H*), 7.95 (t, *J* = 8.0 Hz, 1H, aryl-C*H*), 13.88 (s, 1H, O*H*). ^{13}C NMR (126 MHz, $CDCl_3$) δ 29.75

(C(CH$_3$)$_3$), 31.77 (C(CH$_3$)$_3$), 34.52 (C(CH$_3$)$_3$), 35.47 (C(CH$_3$)$_3$), 47.99 (benzyl-CH$_2$), 111.79, 116.88, 118.29, 118.63, 121.42, 121.56, 123.50, 126.41, 127.01, 127.08, 128.71, 130.52, 130.61, 137.79, 139.12, 139.54, 140.26, 146.02, 156.18, 156.20, 158.35 (aryl-C). HRMS (FAB+) m/z: calcd for $C_{32}H_{36}ON_2$ $[M]^+$ 464.2828; found 464.2817.

L3-MOM (^{Ad}NNO-MOM). Followed the previously reported procedure for **L1-MOM** starting from *N*-Adamant-1-yl-2-bromoaniline.[4] Precipitate forms while stirring overnight. Crude yield: 62% golden foamy oil; some impurities were subsequently removed following deprotection. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 (s, 9H, C(CH_3)$_3$), 1.51 (s, 9H, C(CH_3)$_3$), 1.57 – 1.75 (m, 6H, Ad-CH_2), 1.90 (dd, J = 7.1, 2.9 Hz, 6H, Ad-CH_2), 1.99 – 2.16 (m, 3H, Ad-CH), 3.30 (s, 3H, CH$_2$OCH_3), 4.56 (s, 2H, CH_2OCH$_3$), 7.12 – 7.19 (m, 1H, aryl-CH), 7.22 (ddd, J = 8.6, 7.0, 1.7 Hz, 1H, aryl-CH), 7.34 – 7.42 (m, 1H, aryl-CH), 7.45 (d, J = 2.5 Hz, 1H, aryl-CH), 7.48 (d, J = 2.6 Hz, 1H), 7.56 (dd, J = 7.7, 0.9 Hz, 1H, aryl-CH), 7.61 (ddd, J = 6.8, 5.1, 1.3 Hz, 2H, aryl-CH), 7.78 (t, J = 7.9 Hz, 1H, aryl-CH), 8.35 (s, 1H, NH). ^{13}C NMR (126 MHz, $CDCl_3$) δ 29.77 (Ad-CH), 31.03 (C(CH$_3$)$_3$), 31.69 (C(CH$_3$)$_3$), 34.79 (C(CH$_3$)$_3$), 35.58 (C(CH$_3$)$_3$), 36.66 (Ad-CH$_2$), 43.01 (Ad-CH$_2$), 51.89 (Ad-quat), 57.56 (CH$_2$OCH$_3$), 99.61 (CH$_2$OCH$_3$), 119.35, 120.76, 122.31, 124.86, 126.34, 127.43, 128.86, 129.35, 130.12, 133.97, 136.87, 142.29, 145.82, 151.47, 156.17, 158.29, 159.93 (aryl-C). HRMS (FAB+) m/z: calcd for $C_{37}H_{49}N_2O_2$ $[M + H]^+$ 553.3794; found 553.3790.

L3-H_2 (^{Ad}NNO-H_2). Followed the same procedure as **L2-H_2** except used diethyl ether as the eluent through the SiO_2 plug instead of dichloromethane. An off-white powder precipitated from a hot hexanes solution cooled in the freezer. Yield: 42% off-white powder. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.39 (s, 9H, C(C*H*$_3$)$_3$), 1.49 (s, 9H, C(C*H*$_3$)$_3$)), 1.62 – 1.70 (m, 6H, Ad-C*H*$_2$), 1.98 (d, *J* = 3.0 Hz, 6H, Ad-C*H*$_2$), 2.07 (s, 3H, Ad-C*H*), 5.44 (s, 1H, N*H*), 6.74 (td, *J* = 7.4, 1.1 Hz, 1H, aryl-C*H*), 7.12 (dd, *J* = 8.5, 1.2 Hz, 1H, aryl-C*H*), 7.22 – 7.26 (m, 1H, aryl-C*H*), 7.30 (dd, *J* = 7.6, 1.7 Hz, 1H, aryl-C*H*), 7.39 (dd, *J* = 7.7, 1.0 Hz, 1H, aryl-C*H*), 7.42 (d, *J* = 2.4 Hz, 1H, aryl-C*H*), 7.71 (d, *J* = 2.4 Hz, 1H, aryl-C*H*), 7.86 (d, *J* = 7.6 Hz, 1H, aryl-C*H*), 7.91 (dd, *J* = 8.2, 7.6 Hz, 1H, aryl-C*H*), 13.96 (s, 1H, O*H*). ^{13}C NMR (126 MHz, $CDCl_3$) δ 29.82 (Ad-*C*H), 29.87 (C(*C*H$_3$)$_3$), 31.79 (C(*C*H$_3$)$_3$), 34.52 (*C*(CH$_3$)$_3$), 35.45 (*C*(CH$_3$)$_3$), 36.60 (Ad-*C*H$_2$), 42.57 (Ad-*C*H$_2$), 51.87 (Ad-quat), 115.33, 116.22, 117.82, 118.15, 121.24, 121.90, 124.88, 126.38, 129.69, 131.21, 137.80, 138.93, 139.90, 144.59, 156.49, 156.62, 158.12 (aryl-*C*). HRMS (FAB+) *m*/*z*: calcd for $C_{35}H_{44}ON_2$ $[M]^+$ 508.3454; found 508.3441.

L4-MOM 2-(3,5-di-*t*-butyl-2-(methoxymethoxy)phenyl)-6-(*o*-tolyl)pyridine. An oven-dried 25 mL Schlenk bomb was charged with a stirbar, evacuated and refilled with Ar. Under positive Ar pressure, 0.750 g of 2-bromo-6-(3,5-di-t-butyl-2-(methoxymethoxy)phenyl)pyridine[4], 0.251 g of *o*-tolyl-boronic acid, 0.107 g of Pd(PPh_3)$_4$ and 0.784 g of K_3PO_4 crushed with a mortar and pestle were added and the vessel was sealed with a septum. The vessel was evacuated and refilled with Ar three times, and then 5 mL of dry toluene was added via syringe and the vessel was sealed with a Kontes valve. The reaction mixture was stirred at room temperature for 10 min, then the vessel was placed in a 100 ℃ oil bath for 18 h, then cooled to room temperature, and

the suspension filtered through celite with the aid of Et_2O. Solvent was removed in vacuo and the resulting residue was redissolved in dichloromethane and passed through a SiO_2 plug using 1:9 Et_2O/hexanes as the eluent. 0.742 g (96% crude yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 (s, 9H, C(C*H*$_3$)$_3$), 1.50 (s, 9H, C(C*H*$_3$)$_3$), 2.53 (s, 3H, tolyl-C*H*$_3$), 3.37 (s, 3H, CH_2OCH_3), 4.61 (s, 2H, C*H*$_2$OCH$_3$), 7.28 – 7.34 (m, 3H, aryl-C*H*), 7.38 (dd, *J* = 7.7, 1.0 Hz, 1H, aryl-C*H*), 7.44 (d, *J* = 2.6 Hz, 1H, aryl-C*H*), 7.48 – 7.52 (m, 1H, aryl-C*H*), 7.52 (dd, *J* = 2.6, 0.8 Hz, 1H, aryl-C*H*), 7.69 (dd, *J* = 7.9, 0.9 Hz, 1H, aryl-C*H*), 7.79 (t, *J* = 7.7 Hz, 1H, aryl-C*H*). ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.87 (tolyl-*C*H$_3$), 31.03 (C(*C*H$_3$)$_3$), 31.61 (C(*C*H$_3$)$_3$), 34.73 (*C*(CH$_3$)$_3$), 35.55 (*C*(CH$_3$)$_3$), 57.52 (CH_2O*C*H$_3$), 99.60 (*C*H$_2$OCH$_3$), 122.05, 123.03, 124.96, 125.99, 126.65, 128.35, 129.89, 131.02, 134.23, 136.19, 136.33, 140.54, 142.34, 146.00, 151.36, 157.76, 160.16 (aryl-*C*). HRMS (FAB+) *m*/*z*: calcd for $C_{28}H_{36}O_2N$ $[M + H]^+$ 418.2746; found 418.2726.

L4-H$_2$ 2,4-di-*t*-butyl-6-(6-(*o*-tolyl)pyridin-2-yl)phenol. 0.355 g of **18-MOM** was placed in a 50 mL round bottom flask charged with a stirbar and 20 mL of THF was added to give a colorless solution. The flask was cooled to 0 ℃ with a water-ice bath; a 15 mL solution of 1:1 THF/conc. HCl was added dropwise. The reaction was stirred for 30 min at 0 ℃, then removed from the ice bath and allowed to reach room temperature while stirring, which resulted in the reaction solution turning pale translucent yellow. Stirring was continued overnight, and then the solution was quenched with 2 M aq. NaOH to give a solution with neutral pH. The organic layer was extracted with diethyl ether (3 × 30 mL) and the combined organics were dried over magnesium sulfate and rotovapped

to reveal a yellow oil, which was precipitated from hot hexanes followed by cooling in the freezer to give a pale yellow powder. 0.173 g (54% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.39 (s, 9H, C(C*H*$_3$)$_3$), 1.48 (s, 9H, C(C*H*$_3$)$_3$), 2.42 (s, 3H, tolyl-C*H*$_3$), 7.29 – 7.41 (m, 4H, aryl-C*H*), 7.43 (d, *J* = 2.4 Hz, 1H, aryl-C*H*), 7.46 (dt, *J* = 7.0, 1.4 Hz, 1H, aryl-C*H*), 7.74 (d, *J* = 2.4 Hz, 1H, aryl-C*H*), 7.87 – 7.94 (m, 2H, aryl-C*H*), 14.67 (s, 1H, O*H*). ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.59 (tolyl-*C*H$_3$), 29.71 (C(*C*H$_3$)$_3$), 31.79 (C(*C*H$_3$)$_3$), 34.51 (*C*(CH$_3$)$_3$), 35.45 (*C*(CH$_3$)$_3$), 117.75, 117.95, 120.99, 121.68, 126.18, 126.36, 128.81, 129.73, 131.13, 136.07, 137.80, 137.90, 139.35, 139.79, 156.42, 157.16, 158.55 (aryl-*C*). HRMS (FAB+) *m*/*z*: calcd for $C_{26}H_{31}ON$ $[M]^+$ 373.2406; found 373.2424.

Polymerization of 4 at KFUPM. To the glass reactor of the computer controlled polymerization instrument was added 50 mL of dry toluene, 1 mL triisobutylaluminum, and 24.2 mL 10 wt% MAO in toluene (1000 equiv) at about 10 °C. The temperature was adjusted to 10 °C and the nitrogen was replaced with propylene (2 bar). A 36 mg sample of precatalyst **4** was transferred to a small vial in the Ar-filled glovebox and capped with a septum. The sample was dissolved in 10 mL of toluene and transferred to the reactor against a propylene flow at 10 °C. The reactor was closed, and propylene was rapidly added to give a total volume of approximately 150 mL at 10 °C, whereupon the temperature increased to approx. 20 °C and pressure to approx. 6 bar. Propylene addition was stopped, and stirring increased to 800 rpm, T = 25 °C and p = 7.2 bar (8.2 atm). The reaction was run for 30 min to give approx. 2:1 liquid propylene/toluene. The reactor was vented and opened when most liquid propylene had evaporated. A film of polymer formed on evaporation from the stainless steel pan that we decanted the

toluene and polymer solution into. A solid polymer formed on addition of a couple of mL of methanol. Air drying overnight yielded crude weight of PP of about 14 g. Crude polymer was dissolved in toluene, washed with HCl/methanol (about 1:10) and placed in a separatory funnel. Toluene layer was placed in flask and reduced by half in volume, then transferred to stainless steel pan to evaporate remaining toluene. The polymer did not crystallize. The polymer was further dried under high vacuum overnight to give an oily non-crystalline product.

Polymerization of 4. Reactor Procedures: Propylene polymerizations were conducted in a 1.8 L stainless steel batch reactor. This reactor was manufactured by Buchi AG and sold by Mettler, and is heated/cooled via the vessel jacket and reactor head. Syltherm™ 800 is the heat transfer fluid used and is controlled by a separate heating/cooling skid. Both the reactor and the heating/cooling system are controlled and monitored by a Camile TG process computer. The bottom of the reactor is fitted with a large orifice bottom dump valve, which empties the reactor contents into a 6 L SS dump pot. The dump pot is vented to a 30 gal. blowndown tank, with both the pot and the tank N_2 purged. All chemicals used for polymerization or catalyst makeup are run through purification columns, to remove any impurities that may affect polymerization. The propylene and toluene were passed through 2 columns, the first containing A2 alumna, the second containing Q5 reactant. The N_2 was passed through a single Q5 reactant column. The reactor was cooled to 50℃ for chemical additions. The Camile then controlled the addition of 700 g. of IsoparE, using a micro-motion flowmeter to add accurately the desired amount. The 150 g. of propylene was then added through the

micro-motion flowmeter. The reactor is then preloaded with MMAO to scavenge any impurities in the feeds. After the chemicals are in the reactor, the reactor was heated up to 70℃ for polymerization. The catalyst solution (0.005 M in toluene) is mixed with the desired activator and transferred into the catalyst shot tank. This is followed by 3 rinses of toluene, 5 mL each. Immediately after catalyst addition to the reactor, the run timer begins. For successful polymerizations, exotherm and pressure drops were observed. These polymerizations were run for 15 min., then the agitator was stopped, the reactor pressured up to ~500 psi with N_2, and the bottom dump valve opened to empty reactor contents to the dump pot. The dump pot contents are poured into trays that are set in a vacuum oven, where they are heated up to 140℃ under vacuum to remove any remaining solvent. After the trays cool to ambient temperature, the polymers are weighed for yields and submitted for polymer testing.

Procedure for GPC Analysis. Molecular weight distribution (M_w, M_n) information was determined by analysis on a custom Dow-built Robotic-Assisted Dilution High-Temperature Gel Permeation Chromatographer (RAD-GPC). Polymer samples were dissolved for 90 minutes at 160℃ at a concentration of 30mg/mL in 1,2,4-trichlorobenzene (TCB) stabilized by 300ppm BHT, while capped and with stirring. They were then diluted to 1mg/mL immediately before a 400µL aliquot of the sample was injected. The GPC utilized two (2) Polymer Labs PLgel 10µm MIXED-B columns (300x10mm) at a flow rate of 2.0mL/minute at 150℃. Sample detection was performed using a PolyChar IR4 detector in concentration mode. A conventional calibration of narrow Polystyrene (PS) standards was utilized, with apparent units adjusted to homo-

polyethylene (PE) using known Mark-Houwink coefficients for PS and PE in TCB at this temperature. Absolute M_w information was calculated using a PDI static low-angle light scatter detector.

Procedure for DSC Analysis. Melting and crystallization temperatures of polymers were measured by differential scanning calorimetry (DSC 2910, TA Instruments, Inc.). Samples were first heated from room temperature to 210 ℃ at 10℃ /min. After being held at this temperature for 4 min, the samples were cooled to –40 ℃ at 10/min and were then heated to 215 ℃ at 10/min after being held at –40℃ for 4 min.

Table 1 Crystal data and structure refinement for complexes **1**, **3**, and **6.**

	1	**3**	**6**
CCDC Number	940721	989199	940719
Empirical formula	$C_{46}H_{48}N_2OZr$	$C_{36.83}H_{46.32}Cl_{2.34}N_2OTi$	$C_{40}H_{43}NOTi$
Formula weight	736.08	663.77	601.65
T (K)	100(2)	100(2)	100(2)
a, Å	11.0188(4)	10.387(2)	10.5475(6)
b, Å	13.6909(5)	15.918(4)	11.5064(6)
c, Å	15.0870(6)	21.740(5)	14.7987(8)
α, deg	64.169(2)	76.406(5)	67.224(2)
β, deg	68.942(2)	79.036(5)	86.953(3)
γ, deg	75.522(2)	87.948(5)	76.102(3)
Volume, $Å^3$	1899.90(13)	3429.9(14)	1605.91(15)
Z	2	4	2
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P -1	P -1	P -1
d_{calc}, g/cm^3	1.287	1.285	1.244
θ range, deg	2.0 to 39.6	1.447 to 30.637	2.44 to 41.64
Abs. coefficient, mm^{-1}	0.33	0.463	0.30
Abs. correction	Semi Emp.	Semi Emp.	Semi Emp.
GOF	1.25	1.026	1.71
R_1, wR_2 [I>2σ(I)]	0.0379, 0.0764	0.0387, 0.0950	0.0415, 0.1014

References

[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.

[2] Benzing, E.; Kornicker, W. *Chem. Ber.* **1961**, *94*, 2263-2267.

[3] Felten, J. J.; Anderson, W. P. *J. Organomet. Chem.* **1972**, 36, 87-92.

[4] Klet, R. C.; VanderVelde, D. G.; Labinger, J. A.; Bercaw, J. E. *Chem. Commun.,* **2012**, *48*, 6657–6659.

[5] Würtz, S.; Lohre, C.; Fröhlich, R.; Bergander, K.; Glorius, F. *J. Am. Chem. Soc.* **2009**, *131*, 8344-8345.

[6] Aluri, B. R.; Kindermann, M. K.; Jones, P. G.; Dix, I.; Heinicke, J. *Inorg. Chem.* **2008**, *47*, 6900-6912.