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Preparation of Linear α -Olefins Using Cationic Ni(II)- α -Diimine Catalysts

Supporting Information

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General Considerations. All manipulations of air- and/or water-sensitive compounds were performed using standard high-vacuum or Schlenk techniques. Argon and nitrogen were purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4-Å molecular sieves. Solid organometallic compounds were transferred in an argon-filled Vacuum Atmospheres drybox. ^1H NMR spectra were recorded with either a Bruker WM-250, a Bruker WM-200 or a Varian 400 MHz spectrometer. ^1H NMR spectra of the ethylene oligomers were obtained in CDCl_3 . The oligomer products were also analyzed by gas chromatography (Hewlett Packard 5890A) using a J & W Scientific DB-5 capillary column (30 m, 0.25 mm i.d.) and a flame ionization detector. Temperature profile: isothermal at 35 °C (6 min), 8 °C/ minute, isothermal at 250 °C. GC retention times were compared to that of authentic α -olefin samples ranging from C_6 - C_{18} . Elemental analyses were performed by Oneida Research Services of Whitesboro, NY.

Materials. Toluene, hexane, and diethyl ether were distilled under nitrogen from sodium benzophenone ketyl. Methylene chloride was distilled under nitrogen from P_2O_5 . Chloroform-*d* was dried over 4 Å molecular sieves. Polymer grade ethylene was purchased from Sunox and was used without further purification. A 7% by weight solution of modified MAO (MMAO) was received from Akzo Nobel. The MMAO contained 23% isobutyl aluminoxane. The 2,2'-bipyridine (99%) was purchased from Aldrich and recrystallized from chloroform; resulting crystals were washed with hexane. 1-Nonene was purchased from Aldrich and used without further purification.

$\text{ArN}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{NAr}$ ($\text{Ar}=\textit{p}\text{-MeC}_6\text{H}_4$),³ $\text{PhN}=\text{C}(\text{An})-\text{C}(\text{An})=\text{NPh}$,⁴ $\text{ArN}=\text{C}(\text{R})-\text{C}(\text{R})=\text{NArNiBr}_2$ ² and BipyNiMe_2 were prepared according to modified literature procedures.

Synthesis of Catalyst Precursor

Preparation of the following ligands and nickel dihalides was based on a modified literature procedure.² ($\text{DAB}(\text{R}) = \text{N}=\text{C}(\text{R})-\text{C}(\text{R})=\text{N}$)

$(\text{ArN}=\text{C}(\text{An})-\text{C}(\text{An})=\text{NAr})\text{NiBr}_2$ ($\text{Ar} = \text{C}_6\text{H}_5$) (1). $(\text{C}_6\text{H}_5)_2\text{-DAB}(\text{An})$ (465 mg, 1.4 mmol) and $(\text{DME})\text{NiBr}_2$ (400 mg, 1.3 mmol) were combined and then dissolved in 25 mL of CH_2Cl_2 in a Schlenk tube under an argon atmosphere. The resulting brown mixture was stirred for 18 hours. The solvent was evaporated under reduced pressure to give a brown solid. The product was washed with 2 x 10 mL of Et_2O and dried *in vacuo*. The product was isolated as a brown powder (0.6 g, 90% yield). Anal. Calcd. for $\text{C}_{24}\text{H}_{16}\text{N}_2\text{Br}_2\text{Ni}$: C, 52.32; H, 2.91; N, 5.09. Found C, 52.78; H, 3.64; N 5.27.

$(\text{ArN}=\text{C}(\text{CH}_3)-\text{C}(\text{CH}_3)=\text{NAr})\text{NiBr}_2$ ($\text{Ar} = \textit{para}\text{-Me- C}_6\text{H}_4$) (2). $(\textit{p}\text{-Me- C}_6\text{H}_4)_2\text{-DAB}(\text{CH}_3)$ (370 mg, 1.4 mmol) and $(\text{DME})\text{NiBr}_2$ (400 mg, 1.3 mmol) were combined and then dissolved in 20 mL of CH_2Cl_2 in a Schlenk tube under an argon atmosphere. The resulting brown mixture was stirred for 6 hours. The solvent was evaporated under reduced pressure resulting in a brown solid. The product was washed with 2 x 10 mL of Et_2O and dried *in vacuo*. The product was isolated as a brown powder (0.45 g, 75% yield). Anal. Calcd. for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{Br}_2\text{Ni}$: C, 44.77; H, 4.15; N, 5.80. Found C, 45.13; H, 4.43; N 5.85.

$(2,2'\text{-bipyridine})\text{NiBr}_2$ ⁵ (3). 2,2'-Bipyridine (109 mg, 0.7 mmol) and $(\text{DME})\text{NiBr}_2$ (200 mg, 0.65 mmol) were combined and then dissolved in 25 mL of CH_2Cl_2 in a Schlenk tube under an argon atmosphere. The resulting mixture was stirred for 20 hours. Evaporation of the solvent under reduced pressure gave a pale green solid. The product was washed with 2 x 10 mL of Et_2O and dried *in vacuo*. The product was isolated as a pale green powder (0.19 g, 80% yield).

$[(2,2'\text{-Bipyridine})\text{NiMe}(\text{NCMe})]\text{BAF}$ { $\text{BAF} = [\text{B } 3,5\text{-C}_6\text{H}_3\text{-(CF}_3)_2]_4$ } . A mixture of BipyNiMe_2 (186.0 mg, 0.7593 mmol) and $\text{H}(\text{OEt}_2)_2\text{BAF}$ (768.8 mg, 0.7593 mmol) was placed in a Schlenk tube under an argon atmosphere and cooled to -78°C . Et_2O (20 mL) was then added to the cold flask via syringe, and the reaction mixture was allowed

to warm to rt and stirred for 0.5 h at rt. The reaction mixture was filtered to give a clear yellow solution. Acetonitrile (5 mL) was added via syringe to the solution and the solvents were then removed in vacuo to yield a foam. Hexane (125 mL) was added to the foam and the resulting suspension was stirred vigorously. The hexane was decanted off of the powder, which was then dissolved in 25 mL of CH_2Cl_2 . The CH_2Cl_2 solution was filtered and the solvent was removed in vacuo to give a slightly oily product. The product was obtained as a yellow powder by dissolving it in Et_2O and removing the Et_2O in vacuo. The powder (677.0 mg, 78.61%) was pumped dry on a Schlenk line and stored under argon at $-30\text{ }^\circ\text{C}$: ^1H NMR (CD_2Cl_2 , 400 MHz, rt) δ 8.29 (d, 1, $J = 5.6$, H_{aryl}), 8.21 (d, 1, $J = 5.0$, H_{aryl}), 8.05 (m, 2, H_{aryl}), 7.97 (d, 1, $J = 8.1$, H_{aryl}), 7.92 (d, 1, $J = 7.7$, H_{aryl}), 7.74 (s, 8, BAF: H_o), 7.56 (s, 4, BAF: H_p), 7.52 (m, 2, H_{aryl}), 2.40 (br s, 3, NCMe), 0.34 (s, 3, NiMe); ^{13}C NMR (CD_2Cl_2 , 100 MHz, rt) δ 162.1 (q, $J_{\text{CB}} = 43.2$, BAF: C_{ipso}), 156.7, 152.7, 149.8, 148.0, 140.8, 140.7, 127.7, 127.3, 122.2 and 121.7 (Bipy), 135.2 (BAF: C_o), 129.3 (q, $J_{\text{CF}} = 31.6$, BAF: C_m), 126.3 (q, $J_{\text{CF}} = 272.6$, BAF: CF_3), 117.9 (BAF: C_p), -2.4 (NiMe), (NCMe resonances broad and in the baseline); Anal. Calcd for ($\text{C}_{24}\text{H}_{26}\text{BF}_2\text{N}_3\text{Ni}$): C, 47.65%; H, 2.31%; N, 3.70%. Found: C, 47.39%; H, 2.14%; N, 3.70%.

Oligomerization of Ethylene: Representative Procedures

Oligomerization of Ethylene Using 1 + MMAO (Table 1, entry 5). A 12-mg (0.022 mmol) sample of $[\text{Ph}_2\text{DAB}(\text{An})]\text{NiBr}_2$ was placed in a Parr[®] 1000 mL stirred autoclave under an argon atmosphere with 200 mL of dry toluene. The reactor was purged with ethylene and heated to $55\text{ }^\circ\text{C}$. 2 mL (~ 100 equiv) of a 7% MMAO solution in heptane was added to the suspension. The autoclave was rapidly pressurized to 800 psig and the reaction was stirred for 60 minutes (an exotherm was observed). The oligomerization was quenched upon addition of acetone and water. The solvent was removed *in vacuo* resulting in 50 g (corrected for loss of C_4 , C_6 , and C_8 during work-up; apparent TOF = $81,000/\text{h}$)⁶ of ethylene oligomers (distribution of α -olefins). ^1H -NMR (CDCl_3) and GC analysis: 90% α -olefin (NMR), 93% α -olefin (GC). $\alpha = 0.65$ ⁷

Oligomerization of Ethylene Using 2 + MMAO (Table 1, entry 10). A 14-mg (0.029 mmol) sample of $[(p\text{-Me-Ph})_2\text{DABMe}_2]\text{NiBr}_2$ was placed in a Parr[®] 1000 mL stirred autoclave under an argon atmosphere with 200 mL of dry toluene. The reactor was purged with ethylene and heated to $55\text{ }^\circ\text{C}$. 2.5 mL (~ 100 equiv) of a 7% MMAO solution in heptane was added to the suspension. The autoclave was rapidly pressurized to 800 psig and the reaction was stirred for 60 minutes (exotherm was observed). The oligomerization

was quenched upon addition of acetone and water. The solvent was removed *in vacuo* resulting in 70 g (corrected for loss of C₄, C₆, and C₈ during work-up; apparent TOF = 87,000/h) of ethylene oligomers (distribution of α -olefins). Also a small amount (2 g) of insoluble waxy higher molecular weight oligomers were also isolated. ¹H-NMR (CDCl₃) and GC analysis: 85% α -olefin (NMR), 87% α -olefin (GC). α = 0.59.

Oligomerization of Ethylene Using 3 + MMAO (Table 1, entry 13). A 8-mg (0.021 mmol) sample of (2,2'-bipyridine)NiBr₂ was placed in a Parr[®] 1000 mL stirred autoclave under an argon atmosphere with 200 mL of dry toluene. The reactor was purged with ethylene and heated to 55 °C. 2 mL (~ 100 equiv) of a 7% MMAO solution in heptane was added to the suspension. The autoclave was rapidly pressurized to 800 psig and the reaction was stirred for 60 min (an exotherm was observed). The oligomerization was quenched upon addition of acetone and water. The solvent was removed *in vacuo* resulting in 36.9 g (corrected for loss of C₄, C₆, and C₈ during work-up; apparent TOF = 63,000/h) of ethylene oligomers (distribution of α -olefins). ¹H-NMR (CDCl₃) and GC analysis: 55% α -olefin (NMR), 50% α -olefin (GC). α = 0.57.

Oligomerization of Ethylene Using 3 + MMAO (1-Nonene Control Experiment). A 15-mg (0.04 mmol) sample of (2,2'-bipyridine)NiBr₂ was placed in a Parr[®] 1000 mL stirred autoclave under an argon atmosphere with 200 mL of dry toluene and 2 mL of 1-nonene. The reactor was purged with ethylene and heated to 35 °C. 2 mL (~ 100 equiv) of a 7% MMAO solution in heptane was added to the suspension. The autoclave was rapidly pressurized to 800 psig and the reaction was stirred for 60 minutes (an exotherm was observed). The oligomerization was quenched upon addition of acetone and water. GC analysis of the resulting oligomers showed no isomerization of the authentic sample of 1-nonene.

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(6) Calculation of turnover frequency: Turnover frequencies are calculated from oligomer productivity. Productivities are corrected for loss of C₄, C₆, C₈, and some C₁₀ (GC analysis). GC analysis of the crude mixture (immediately following reaction) relative to the GC analysis of the isolated oligomers allows for the mass of C₆, C₈, and C₁₀ lost during work-up to be determined. Due to overlapping solvent signals in the GC analysis, loss of C₄, C₆, and C₈ are often determined from α .

(7) Calculation of α :

$$\alpha = \frac{\text{moles of } C_{n+2}}{\text{moles of } C_n} = \frac{\text{moles } C_{14}}{\text{moles } C_{12}}$$

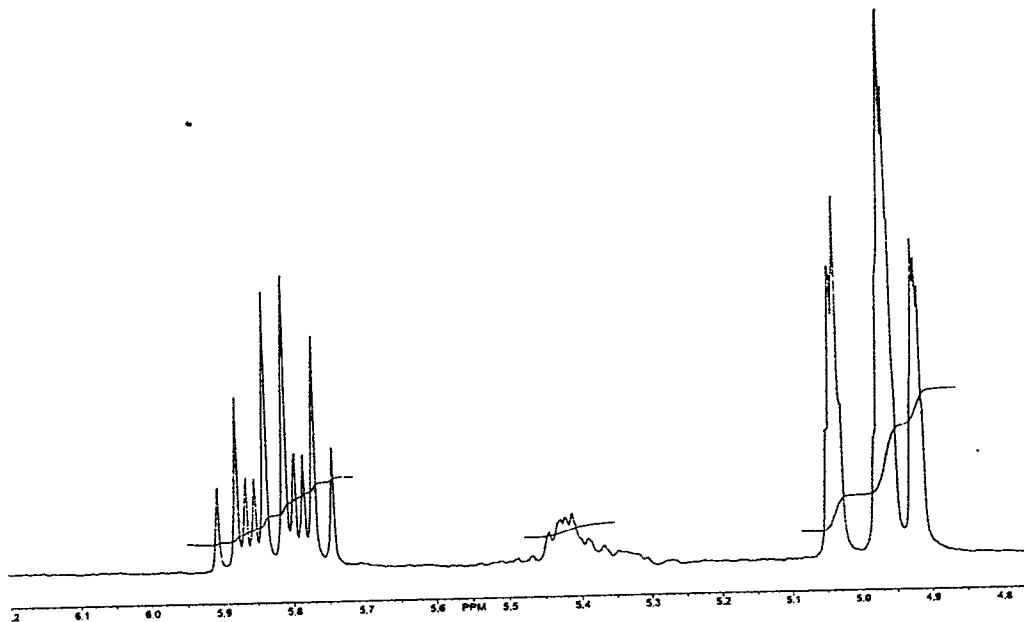
e.g. Table 5.1, entry 1

$$\alpha = \frac{0.0159}{0.0225} = 0.71$$

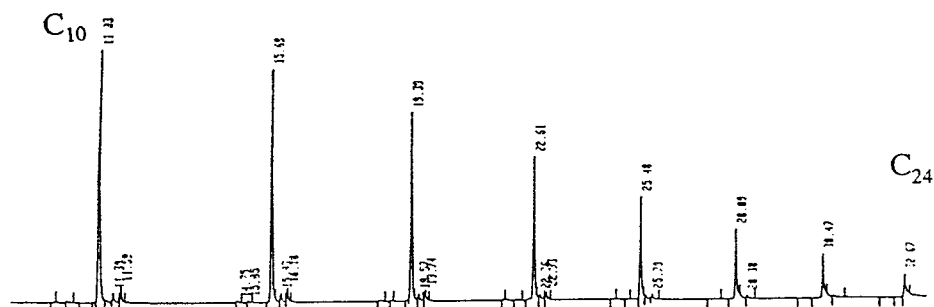
– C₁₂ and C₁₄ oligomers were chosen for the α calculation because the GC peaks are well resolved and of significant area.

POOR QUALITY ORIGINAL

^1H NMR spectrum of oligomers: 1/MMAO, 35 °C, 800 psig (Table 1, entry 2)

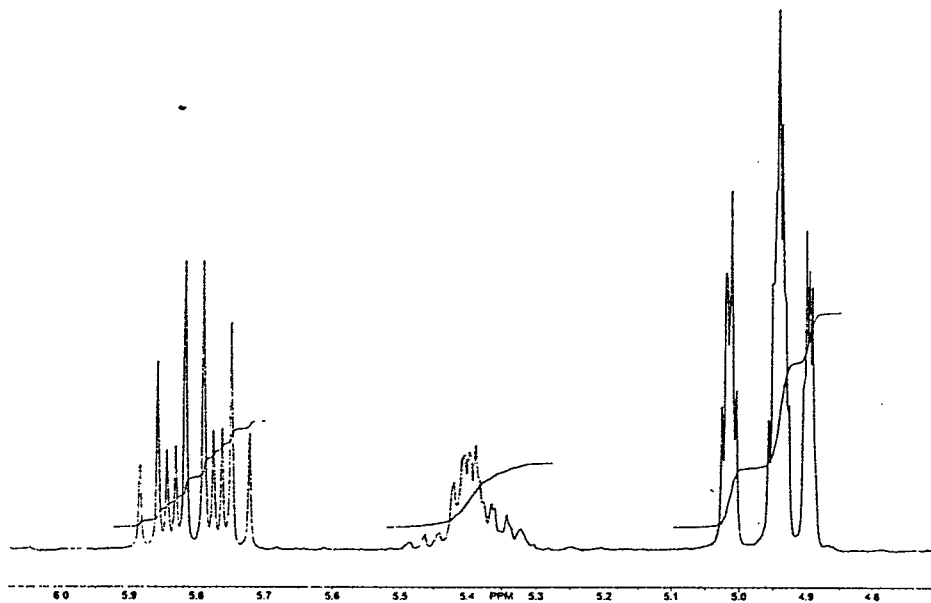


GC trace of oligomers: 1/MMAO, 35 °C, 800 psig (Table 1, entry 2)

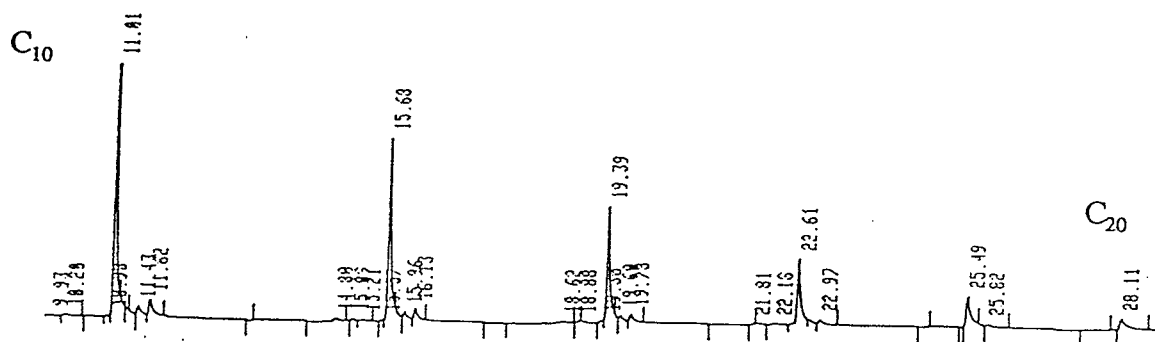


POOR QUALITY ORIGINAL

^1H NMR spectrum of oligomers: 2/MMAO, 75 °C, 800 psig (Table 1, entry 11)

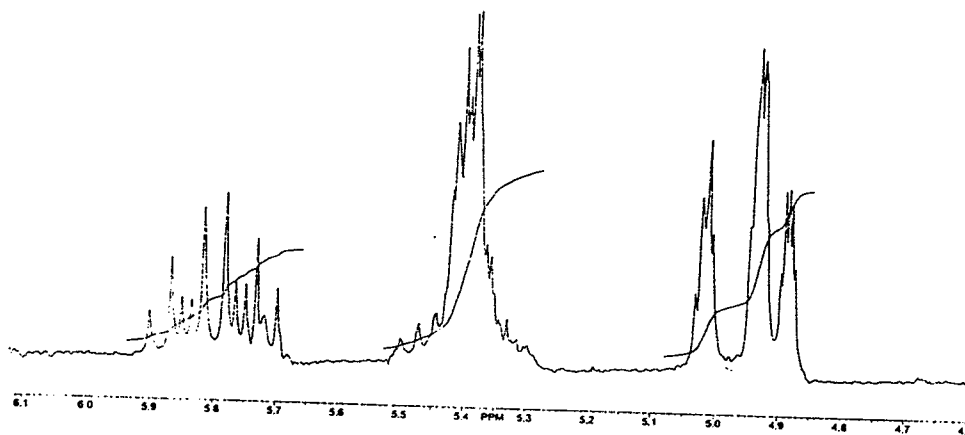


GC trace of oligomers: 2/MMAO, 55 °C, 800 psig (Table 1, entry 10)

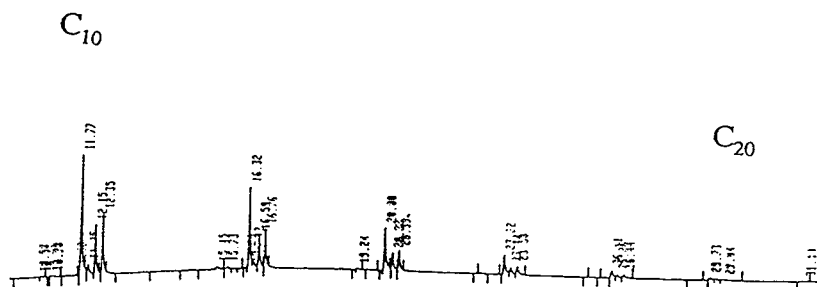


POOR QUALITY ORIGINAL

^1H NMR spectrum of oligomers: 3/MMAO, 75 °C, 800 psig (Table 1, entry 14)



GC trace of oligomers: 3/MMAO, 75 °C, 800 psig (Table 1, entry 14)



POOR QUALITY ORIGINAL

GC trace of oligomers isolated 1-nonene control experiment: 3/MMAO, 35 °C, 56 atm psig

