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Ethylene Oligomerization and Propylene Dimerization Using Cationic (α-Diimine)nickel(II) Catalysts

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Nickel-catalyzed ethylene oligomerization and propylene dimerization reactions are described. A series of aryl-substituted α-diimine ligands **1** (ArN═C(R)C(R)═NAr, R,R ≡ 1,8-naphth-diyl, Ar ≡ XC_6H_4, X = *p*-CF_3 (**a**), *p*-H (**b**), *p*-Me (**c**), *p*-OMe (**d**), *o*-Me (**e**)) and their corresponding Ni(II) dibromide complexes **2** were prepared. Treatment of the Ni(II) dibromide complexes **2** with aluminum alkyl activators such as MAO (methylalumoxane), modified MAO (MMAO), or Et_2AlCl in toluene generates active cationic catalysts *in situ* that oligomerize ethylene to a Schulz−Flory distribution of linear α-olefins. Reaction conditions can be adjusted that lead to selectivities as high as 96% for linear α-olefins. These catalysts are highly active, with ethylene turnover frequencies as high as 1.4×10^5 mol of C_2H_4/((mol of Ni)h) observed. Schulz−Flory α values range from 0.59 to 0.81 and are dependent on the reaction temperature, ethylene pressure, and nature of the aluminum cocatalyst. The active catalysts dimerize propylene, generating product mixtures that have roughly equal compositions of *n*-hexenes and 2-methylpentenes. 2,3-Dimethylbutenes are minor products, usually comprising less than 10% of the total product distribution. Propylene dimers and their associated isomerization products are the only reaction products observed under the standard reaction conditions used. Propylene turnover frequencies as high as 2×10^4 mol of C_3H_6/((mol of Ni)h) were observed. Control experiments indicate that terminal olefins are slowly isomerized to internal olefins under propylene dimerization reaction conditions but dimer production is fast relative to product isomerization. Higher olefins such as 1-butene and 4-methyl-1-pentene are dimerized very slowly by these catalysts.

Introduction

Transition-metal-catalyzed oligomerization of ethylene and dimerization of α-olefins are important processes that are used to convert these basic feedstocks into useful value-added products. Ethylene oligomerization by nickel catalysts is the first step of the Shell Higher Olefin Process (SHOP).[1−4] The SHOP process is highly selective for producing linear α-olefins in the C_4−C_{20+} range, which are used as comonomers to synthesize linear low-density polyethylene and in the production of lubricants, plasticizers, surfactants, and detergents.[5] The IFP Dimersol process utilizes a cationic nickel catalyst to nonselectively dimerize and codimerize propylene and 1-butene; the dimer products are used as gasoline additives.[6−8]

Olefin dimerization[9] and oligomerization[10] reactions are typically carried out using homogeneous late-transition-metal catalysts, particularly nickel-based catalysts. A wide variety of ligands have been employed successfully with these systems,[11−20] and careful tuning of ligands can be used to vary product composition from lower oligomers to polymer.[21−24] Neutral nickel catalysts based on phosphorus−oxygen chelates are particularly

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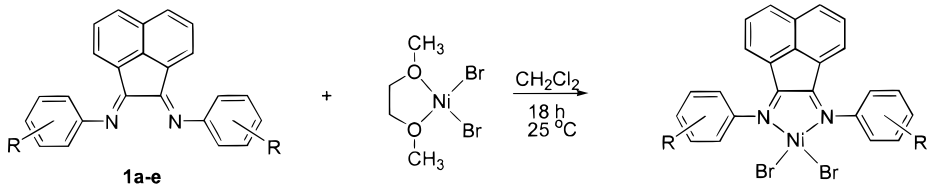
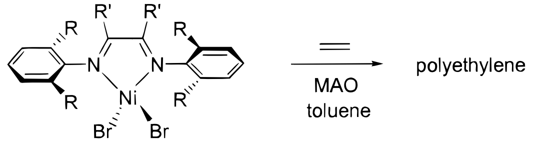
Scheme 1. α-Diimine Ligands 1a−e and Synthesis of Corresponding Nickel(II) Dibromide Complexes 2a−e



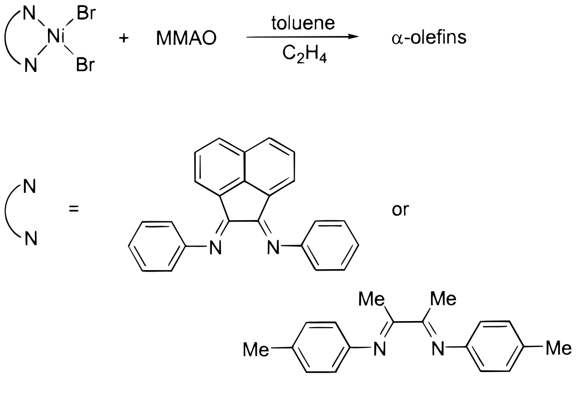
2a $R = 4\text{-}CF_3$
2b R = 4-H
2c R = 4-Me
2d R = 4-OMe
2e R = 2-Me

well-developed and are employed in industrial SHOP reactors.[3,4,25] A series of extremely active Ni(II) ethylene oligomerization catalysts containing dithioacetylacetonate chelating ligands have been reported,[26−28] and the mechanism by which they dimerize propylene has been investigated.[29] Recently, we reported highly active iron-based catalysts for ethylene oligomerization.[30]

The strong propensity of late-transition-metal-based catalysts to undergo β-hydrogen elimination reactions has largely relegated this class of catalysts to applications in dimerization or oligomerization processes. We recently reported the development of cationic Ni(II) and Pd(II) α-diimine complexes that *polymerize* ethylene and α-olefins (eq 1).[31,32] The key to the ability of these late-transition-metal catalysts to form polymer lies in the steric bulk of the α-diimine ligands. The aryl rings of the α-diimine ligands are approximately orthogonal to the plane formed by the metal and coordinated nitrogen atoms. This ring orientation places the bulky substituents in axial sites, which effectively retards the rate of chain transfer relative to chain propagation. In a recent communication we reported that when diimine ligands lacking bulky aryl *ortho* substituents are used, the resulting Ni(II)-based systems produce a Schulz−Flory distribution of ethylene oligomers (eq 2).[33] We have subsequently undertaken a series of detailed studies investigating the electronic effects of the α-diimine ligand on the oligomerization of ethylene. In addition, the effects of the aluminum alkyl cocatalyst on catalyst activity, catalyst lifetime, and product composition have been examined. We have discovered that these sterically unhindered Ni(II) catalysts dimerize propylene and have investigated the effects of α-diimine ligand electronics coupled with variations in reaction conditions on the dimer product distribution. Proposed mechanisms for both ethylene oligomerization and propylene dimerization are discussed.



R = *i*-Pr
R' = H, Me, or R', R' = 1,8-naphth-diyl



(2)

Results and Discussion

A. Catalyst Preparation. Extensive studies on the synthesis and reactivity of a wide variety of d^8 α-diimine complexes have been reported by Elsevier et al.[34−38] Using similar synthetic methods, a series of *p*-aryl-substituted α-diimine ligands and their corresponding nickel(II) dibromide complexes were prepared as shown in Scheme 1. Synthesis and characterization of ligands **1b−e** and nickel(II) dibromide complexes **2b−e** have been previously reported.[37,39,40] Acenaphthoquinone and slightly more than 2 equiv of the appropriate aniline were combined in toluene containing camphorsulfonic

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Table 1. Oligomerization of Ethylene in 200 mL of Toluene with 2/Al Cocatalyst[a]

entry no.	catalyst	press. (atm)	temp (°C)	time (min)	TON[b] × 10^{-3}	% α-olefin[c]	Schulz−Flory α
1	**2a**/MMAO	1	35	60	22	57	0.50
2	**2a**/MMAO	15	35	60	116	81	0.59
3	**2a**/MMAO	28	35	60	136	87	0.61
4	**2a**/MMAO	56	35	60	113	91	0.68
5	**2a**/MMAO	56	15	60	26	94	0.71
6	**2a**/MMAO	56	55	60	103	88	0.66
7	**2a**/MMAO	56	75	60	74	88	0.63
8	**2b**/MMAO	56	35	60	49	92	0.70
9	**2c**/MMAO	56	35	60	45	91	0.71
10	**2d**/MMAO	15	35	60	102	84	0.64
11	**2d**/MMAO	28	35	60	114	88	0.67
12	**2d**/MMAO	56	35	60	50	95	0.74
13	**2a**/MMAO	28	35	30	65	94	0.68
14	**2a**/MAO	28	35	30	80	94	0.68
15	**2a**/MAO-IP	28	35	30	23	96	0.67
16	**2a**/Et_2AlCl	28	35	30	51	90	0.81

[a] Reaction conditions: entries 1−12, [Ni] = 1.00×10^{-4} M, 240 equiv of Al/equiv of Ni; entries 13−16, [Ni] = 2.50×10^{-5} M, 200 equiv of Al/equiv of Ni. [b] Turnover number = mol of ethylene consumed/mol of Ni catalyst. [c] Remainder of product is 2-alkenes.

acid (ca. 2−3 mol %), and the mixture was heated to reflux. Water evolution was observed by collecting the toluene/water azeotrope using a Dean−Stark trap. Electron-rich anilines react smoothly under these conditions to form the corresponding diimines, but even at these temperatures the reaction using electron-poor 4-(trifluoromethyl)aniline is sluggish. Efforts to prepare the diimine derived from 4-nitroaniline and acenaphthoquinone using these reaction conditions proved unsuccessful. Crude ligands were purified via precipitation from chloroform with pentane, followed by several pentane washes.

The nickel(II) dibromide complexes **2a**−**e** were prepared from the ligands **1a**−**e** by reaction of a slight excess of the free diimine ligand with (1,2-dimethoxyethane)nickel(II) bromide in methylene chloride (Scheme 1). The nickel complexes precipitated from solution and were purified by washing away the 1,2-dimethoxyethane and excess ligand with diethyl ether. Complexes **2a**−**e** are air-stable solids and are insoluble in common organic solvents, including CH_2Cl_2, $CHCl_3$, Et_2O, toluene, and hydrocarbon solvents. They are sparingly soluble in 1,2-difluorobenzene.

B. Oligomerization of Ethylene. Treatment of catalyst precursors **2a**−**d** with MAO, modified MAO (MMAO), MAO-IP,[41] or Et_2AlCl in toluene generates active ethylene oligomerization catalysts. The results of a series of these oligomerization reactions are summarized in Table 1. A Schulz−Flory distribution[42−45] of oligomers is produced, which is characterized by a constant, α, where α represents the probability of chain propagation (eq 3). An oligomer distribution with a small Schulz−Flory α (e.g. $\alpha < 0.5$) will therefore consist mainly of dimers and lower oligomers, while the bulk of an oligomer distribution with a high Schulz−Flory α (e.g. $\alpha > 0.8$) will consist of higher oligomers. The olefins produced are primarily linear α-olefins, with the remainder consisting of linear 2-alkenes. Branched olefins are not observed when reaction times are 1 h or less. Very long reactions (e.g. 3 h or more) with the most active catalysts occasionally have very small amounts of branched products present (<2% of total products), which we believe are formed from reincorporation of oligomerization products that build to high concentrations after long reaction periods.

$$\alpha = \frac{\text{rate of propagation}}{\text{rate of propagation} + \text{rate of chain transfer}} = \frac{\text{moles of } C_{n+2}}{\text{moles } C_n} \tag{3}$$

The oligomerization mechanism is proposed to be that shown in Scheme 2 and is similar to that proposed for polymerization using analogous Ni(II) complexes.[31] Evidence suggests the intermediate cationic nickel alkyl complexes exist as β-agostic species.[46−48] Metal migration along the chain occurs as shown through olefin hydride species such as **III**.[49] When chain transfer occurs from species **II**/**III**, only α-olefins can be produced. Internal olefins (2-alkenes) can be produced only when chain transfer occurs from secondary alkyl agostic species **IV**/**IV′** (α-olefins could arise from these species as well). We have suggested that chain transfer may occur through associative displacement of olefin from an olefin hydride species such as **III**. Theoretical calculations suggest that chain transfer may occur via a direct β-H migration from the alkyl group to bound ethylene in a species such as **I**.[50,51] No experimental evidence is currently available which distinguishes these possible chain transfer mechanisms.

Some general trends are observed in the data in Table 1, particularly the effects of ethylene pressure and temperature, which can be rationalized with the mechanism shown in Scheme 2. Increasing the ethylene pressure results in an increase in the selectivity for α-olefins, as well as an increase in the Schulz−Flory α constant (entries 1−4, 10−12, Table 1). According to Scheme 2, an increase in ethylene concentration (pressure) should favor increased selectivity for α-olefins over internal olefins because the rate of chain transfer from species **II**/**III** relative to the rate of chain isomerization to species **IV**/**IV′** increases with increasing ethylene concentration. The fact that the Schulz−Flory α values decrease with decreasing $[C_2H_4]$ suggests that the ratio of chain transfer to propagation (k_{ct}/k_p) is much greater for secondary alkyl complexes **IV**/**IV′** than for primary alkyl species **II**. This is supported by the observation that no branched α-olefins are produced and all internal olefins produced are 2-alkenes (*cis*- and *trans*-$CH_3CH{=}CHR$). These observations suggest that once metal migration occurs to give **IV**/**IV′** no ethylene insertion occurs and no further metal migration occurs. Thus, the secondary alkyl species **IV**/**IV′** either undergo chain

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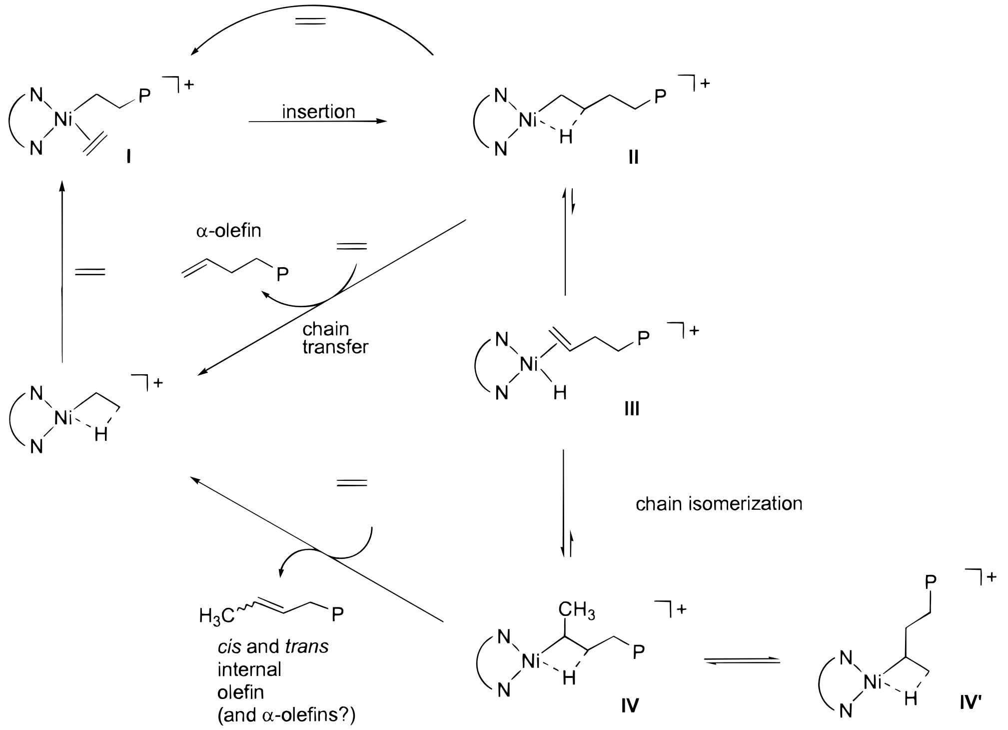
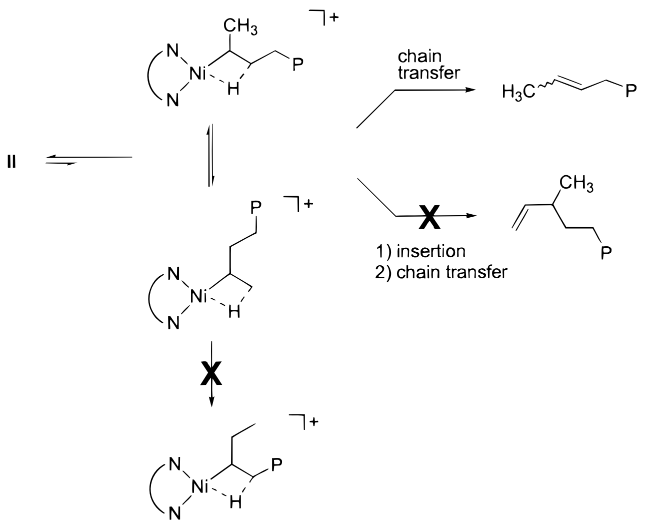
Scheme 2. Proposed Mechanism of Olefin Oligomerization



Scheme 3. Proposed Mechanism of Chain Isomerization/Transfer for Secondary Alkyl Species



transfer or isomerize back to **II,** as shown in Scheme 3. Schulz–Flory α values should track the percentage of α-olefin produced. Inspection of Table 1 shows that this trend is followed, with the exception of the oligomerization carried out with Et_2AlCl as activator (run 16; this activator behaves differently from MAO activators, see below).

Turnover frequencies are also ethylene-dependent, reaching a maximum value when the ethylene pressure is near 30 atm. Further increases in ethylene pressure result in a decrease in the apparent turnover frequency. The reason for this decrease in turnover frequency is not understood. Possibilities include a decrease in the solvent polarity at higher ethylene concentrations[52,53] or inhibition due to formation of an inactive (or less active) five-coordinate intermediate.

In addition to ethylene pressure effects, the oligomerization reaction is strongly affected by the temperature. As the temperature is increased, both selectivity for α-olefins and the Schulz–Flory constant α decrease (entries 4–7, Table 1). These results indicate that the rate of chain transfer relative to the rate of chain propagation increases with temperature. Since ethylene solubility in toluene decreases with increasing temperature,[54] the loss of selectivity for α-olefins and concomitant decrease in the Schulz–Flory α constant as the temperature increases could be due in part to lower concentrations of ethylene in solution. Thus, the same arguments given for ethylene pressure effects on these parameters apply to the observed temperature effects. Furthermore, the first-order chain isomerization reaction of **II** should show a stronger temperature dependence than the second-order reaction with ethylene required to effect chain transfer. This same trend is seen with increased branching of polyethylene as the temperature is increased at constant pressure.[31] Turnover frequencies also increase with temperature (compare entries 4 and 5), but significant catalyst decomposition occurs over 60 min when the reaction temperature is raised above 55 °C (compare entries 6 and 7 with entry 4).

No substantial ligand electronic effects on selectivity for α-olefins or the Schulz–Flory α constant are observed. There does appear to be a trend of increasing turnover frequencies as the metal center becomes more electrophilic. For example, as the para substituents on

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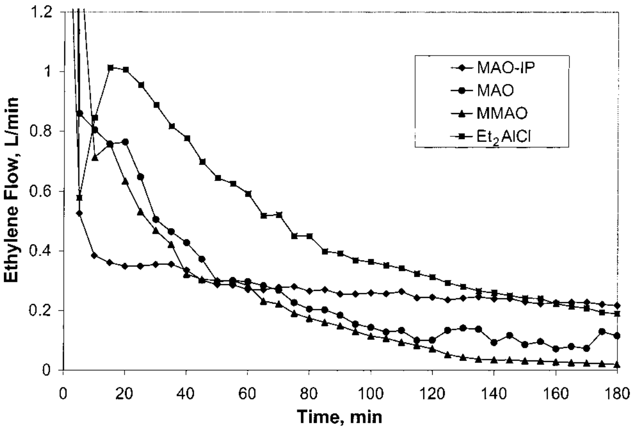

Figure 1. Ethylene flow profiles in oligomerization reactions with **2a** and various cocatalysts (400 equiv of Al/equiv of Ni, 15 atm of ethylene, 35 °C).

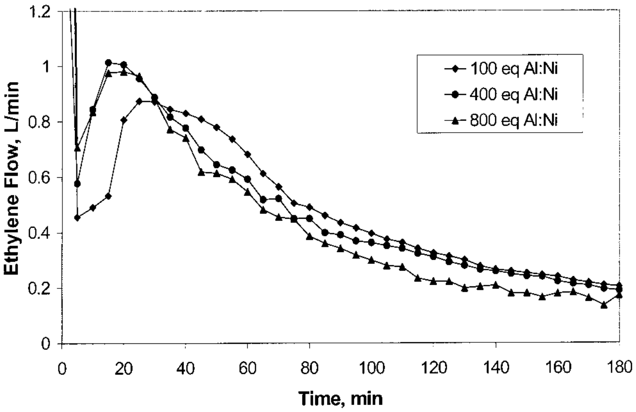

Figure 2. Ethylene flow profiles in oligomerization reactions with various ratios of **2a** to Et_2AlCl (15 atm of ethylene, 35 °C).

the ligand aryl groups are varied from methyl to trifluoromethyl, turnover frequencies double (entries 4, 8, 9, Table 1). The electron-poor trifluoromethyl substituent is expected to lead to a more electrophilic metal center relative to that when more electron-rich substituents are present, which leads to an increased rate of ethylene insertion, the turnover-limiting step. However, the methoxy substituent leads to turnover frequencies that are higher than expected (entries 10−12, Table 1). The reason for this behavior is not clear, but formation of Lewis acid−base complexes of the methoxy group with excess aluminum cocatalyst would be expected to reduce electron density on the ligand and therefore lead to a more electrophilic metal center than would normally be expected.

The choice of aluminum cocatalyst has a significant effect on the ethylene oligomerization reactions. MAO, MMAO, MAO-IP, and Et_2AlCl are all effective cocatalysts. Reactions activated by MAO, MMAO, and MAO-IP all show similar Schulz−Flory values, but those activated by Et_2AlCl produce oligomer mixtures with a higher Schulz−Flory α constant (entries 13−16, Table 1).

Catalyst lifetimes were investigated by measuring the ethylene flow into the reactor with a mass flowmeter. The lifetimes of catalysts generated by activation of **2a** with various cocatalysts in ethylene oligomerization reactions are shown in Figure 1. The high ethylene flow rates indicated during the initial 5−10 min of each reaction reflect the process of ethylene saturation of the toluene solvent. Overall, Et_2AlCl generates the most active catalyst over 3 h reaction periods. However, comparison of entries 13−16 (Table 1) shows that, over the first 30 min, the MAO-activated catalyst, for example, produces more turnovers than the Et_2AlCl-activated catalyst. Judging from the flow profiles (Figure 1), this is likely due to a more rapid catalyst activation by MAO and thus more turnovers at early times. MAO and MMAO cocatalysts produce catalysts that are most active during the first 20 min of the reaction, after which time catalyst activity steadily declines. After 3 h, the catalyst produced from MMAO is almost completely inactive. MAO-IP generates the least active catalyst during early reaction times, but this catalyst shows more constant activity throughout 3 h reactions than reactions using MAO or MMAO. Longer runs with **2a**/MAO-IP show that the catalyst is still active after 12 h, although the catalyst activity at this point is less than 10% of the activity observed 30 min into the reaction.

The effects of various Al:Ni ratios in ethylene oligomerizations were investigated using **2a** and Et_2AlCl, and the results are shown in Figure 2. Generally, a threshold amount of cocatalyst is needed to effectively activate the precatalyst, presumably to scavenge impurities that may poison the active catalyst. Figure 2 suggests that a period of 15−25 min is required for full activation of the precatalyst using Et_2AlCl, depending on the Al:Ni ratio used. No similar induction period is seen when using MAO-type activators.[55] The activation periods when using Et_2AlCl as the cocatalyst were found to be variable and not well-defined. Since turnover numbers shown in Table 1 were determined by measuring the amount of reaction products formed over set reaction periods, the combination of variable activation periods and catalyst deactivation makes turnover number comparisons between various cocatalysts difficult and very qualitative at best.

Higher amounts of cocatalyst (e.g. >1000 equiv of Al/1 equiv of Ni) in the ethylene oligomerization reactions lead to faster degradation of the active catalyst. The reason for this trend is not understood, but it was observed with all cocatalysts tested. Cavell and Masters noted that contamination of Et_2AlCl with Et_3Al reduced the activity of cationic Ni catalysts in olefin oligomerizations.[26] Similarly, Kissin and Beach have reported that sulfonated nickel ylide ethylene oligomerization catalysts are reduced to inactive Ni(0) species by Et_3Al.[17] Attempts to use Me_3Al to activate dibromide precatalyst **2d** in the presence of ethylene failed to form an active catalyst. These observations may suggest that trialkylaluminum impurities in the cocatalyst could in part be responsible for catalyst degradation.

Adding certain ortho substituents to the aryl rings of the α-diimine ligands leads to much longer-lived catalysts.[56] In addition, the ethylene flow experiments described above show that lower Al:Ni ratios result in

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(55) In addition to the mass flow data, reactions initiated with MAO-type cocatalysts are exothermic at the start of the reaction, while reactions initiated with Et_2AlCl exhibit maximum exotherms 10−20 min after the reaction start.

(56) Svejda, S. A.; Onate, E.; Gates, D. P.; Brookhart, M. Manuscript in preparation.

Table 2. Oligomerization of Ethylene with 2a/MMAO[a]

entry no.	time (min)	TON $\times 10^{-3}$	% α-olefin	Schulz–Flory α[b]
1	15	41	94	0.67
2	30	75	93	0.67
3	60	113	91	0.68
4	120	185	90	0.68

[a] Reaction conditions: [Ni] = 1.00×10^{-4} M, 240 equiv of Al/equiv of Ni, 200 mL of toluene, 56 atm of ethylene, 35 °C. [b] Determined from ratios of 1-tetradecene/1-dodecene GLC areas.

more active and longer-lived catalyst systems. These results seem to indicate that catalytic intermediates formed from precursors containing diimine ligands lacking steric bulk near the metal center could possibly deactivate through reaction with excess cocatalyst.

The oligomer composition and distribution at various points during the reaction was investigated by running a series of ethylene oligomerization reactions catalyzed by **2a**/MMAO using identical reaction conditions but different reaction times. The results are summarized in Table 2. Total turnover numbers are not proportional to reaction time; i.e., turnover frequencies appear to drop as the reaction progresses, which supports the data obtained in the monomer flow measurement experiments, indicating significant catalyst decay occurs in $^1/_2$–2 h. Although catalyst performance degrades with time, selectivity for α-olefins and the Schulz–Flory α value remain essentially unchanged throughout the duration of catalysis. Relatively constant α-olefin to internal olefin ratios indicate no significant isomerization of the reaction products is taking place at longer reaction times, and these data support a previous control experiment where no observable isomerization of added 1-nonene was seen.[33]

C. Dimerization of Propylene. Treatment of precatalysts **2a–e** with MMAO or Et_2AlCl in toluene generates active catalysts which dimerize propylene. The results of a series of propylene dimerization reactions with these catalysts are summarized in Table 3. Under the reaction conditions described in Table 3, these catalysts are greater than 99% selective for production of propylene dimers as determined by GLC. No trimers or higher oligomers are observed in 30 min runs. The products referred to in Table 3 are shown in Scheme 5.

At low propylene concentrations, the turnover frequencies are dependent on the propylene concentration. As the propylene concentration is increased, the turnover frequency becomes independent of propylene concentration (entries 1–5, Table 3). This behavior may be due to an equilibrium between an alkyl agostic resting state species and an alkyl olefin resting state species at lower propylene concentrations. This equilibrium would shift in favor of the alkyl olefin species at higher propylene concentrations. The turnover-limiting step is believed to be migratory insertion of the alkyl olefin complex; therefore, the observed rate of dimerization should be independent of propylene concentration when the sole resting state species is the alkyl olefin species. The dimer product distribution is essentially unaffected by changes in the propylene concentration, although the degree of isomerization of the reaction products decreases with increasing propylene concentration.

Turnover frequencies at 2 atm of propylene pressure increase as the temperature is raised from −15 to 0 °C but decline as the temperature is raised further (entries 2, 6, and 7, Table 3). We believe this observed decrease in turnover frequency is due to a lower concentration of propylene in solution at 28 °C than at 0 °C, since the solubility of propylene in toluene decreases dramatically with increasing temperature.[54] The observation that maximum turnover frequency at 2 atm occurs near 0 °C therefore indicates the point of balance between monomer concentration in solution and the expected increasing rate of insertion with increasing temperature. The product distribution is only slightly affected by temperature changes, but the degree of isomerization of the reaction products was nearly double for reactions run at 28 °C as opposed to those run at −15 °C (compare entries 6 and 7).

Turnover frequencies increase as the electrophilic nature of the catalyst increases (entries 1, 8–10, Table 3). Dimerizations catalyzed by **2a**/MMAO proceed at more than twice the rate as those catalyzed by **2d**/MMAO over the first 30 min following catalyst activation. The dimer product distribution is relatively independent of electronic effects, but the degree of product isomerization increases as the catalyst becomes more electrophilic.

The nature and quantity of aluminum cocatalyst affects the outcome of the propylene dimerization reactions. For example, use of Et_2AlCl as the cocatalyst results in turnover frequencies that are 1 order of magnitude lower than when MMAO is used (compare entries 2 and 11, Table 3). Since long induction periods were observed when Et_2AlCl was used as a cocatalyst in ethylene oligomerizations at 35 °C, it is likely that the apparent low activity of **2a**/Et_2AlCl in dimerizing propylene is due to an even longer induction period, since this reaction was run at 0 °C. While the overall product distribution is essentially unchanged, the degree of isomerization observed when Et_2AlCl is used is substantially lower. Varying the amount of MMAO used led to different turnover frequencies; 1300 equiv of Al/equiv of Ni was found to be the optimal ratio of cocatalyst to precatalyst for maximizing turnover frequency (entries 1, 12–13, Table 3). In contrast, lower cocatalyst:precatalyst ratios led to optimal turnover frequencies in the ethylene oligomerization reactions (see above).

The isomerization of dimer products was probed in a control experiment in which 1-pentene was added to a propylene dimerization reaction catalyzed by **2a**/MMAO (Table 4). Over the course of 2 h, 1-pentene was slowly isomerized to the internal isomers, which suggests that isomerization of the reaction products takes place to some extent after chain transfer. Although isomerization is taking place, it is slow as compared to the rate of dimer production.

Even though some isomerization of the dimerization products takes place during the reaction, some conclusions about the regiochemistry of propylene insertion can be drawn on the basis of product distributions. A commonly advanced mechanism for nickel-catalyzed dimerization assumes a propylene-free nickel hydride

Table 3. Dimerization of Propylene in 50 mL of Toluene with 2/Al Cocatalyst[a]

					product distribn, mol %[b]				
entry no.	catalyst	press. (atm)	temp (°C)	TOF[c]	path A	path B	path C	path D	isomerizn products[d]
1	**2a**/MMAO	1.1	0	4410	19	38	8	21	14
2	**2a**/MMAO	2	0	14600	19	41	9	20	11
3	**2a**/MMAO	3	0	19600	19	42	8	20	11
4	**2a**/MMAO	4	0	19500	18	40	8	23	11
5	**2a**/MMAO	5	0	19400	19	43	8	21	9
6	**2a**/MMAO	2	−15	2760	18	37	8	29	8
7	**2a**/MMAO	2	28	10000	21	38	8	18	15
8	**2b**/MMAO	1.1	0	3730	20	39	9	20	12
9	**2c**/MMAO	1.1	0	3310[e]	24	41	9	16	10
10	**2d**/MMAO	1.1	0	1800	20	38	10	22	10
11	**2a**/Et$_2$AlCl	2	0	1520	19	40	8	25	8
12	**2a**/MMAO[f]	1.1	0	3140[g]	17	34	8	25	16
13	**2a**/MMAO[h]	1.1	0	2640[g]	14	28	8	29	21
14	**2e**/MMAO	1.1	0	230	13	13	6	43	25

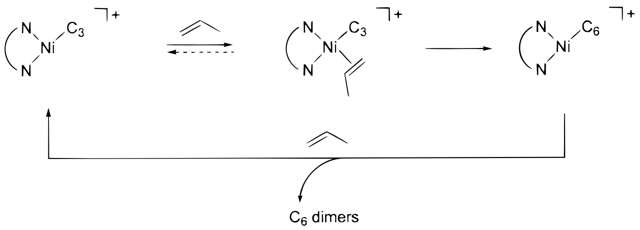
[a] Reaction conditions: 1300 equiv of Al/equiv of Ni; 30 min reaction times. [b] Product distribution according to pathways shown in Scheme 5. [c] TOF = turnover frequency (mol of C_3H_6/((mol of Ni)h)). [d] Percentage of product mixture containing double-bond shift isomers of the dimerization products. [e] 35 min reaction time. [f] 870 equiv of Al/equiv of Ni. [g] 60 min reaction time. [h] 1700 equiv Al/equiv of Ni.

Table 4. Isomerization of 1-Pentene by 2a/MMAO under Propylene Dimerization Conditions[a]

	rel mol %[b]		
isomer	5 min	1 h	2 h
1-pentene	100	79	71
trans-2-pentene	0	12	16
cis-2-pentene	0	9	13

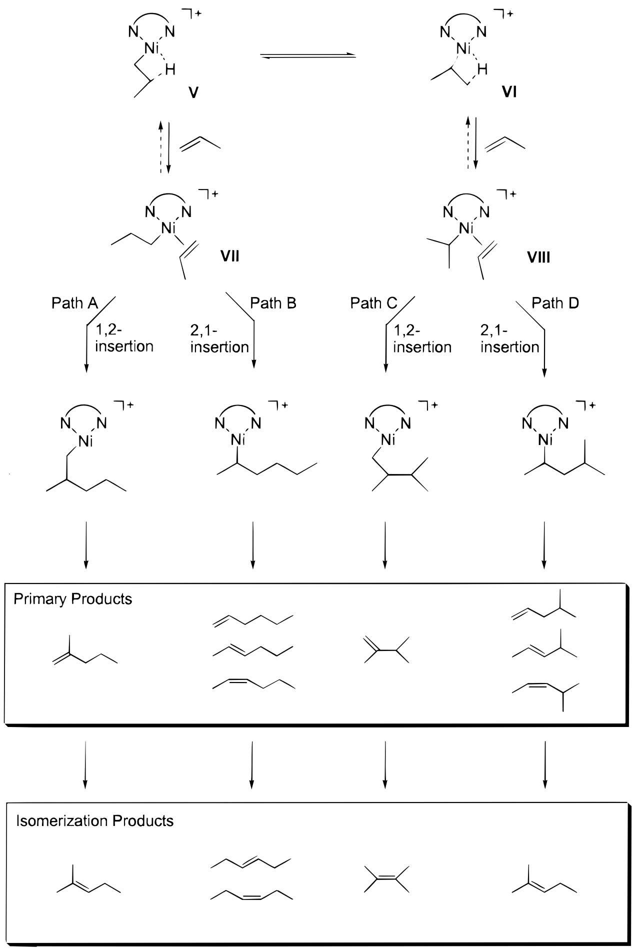
[a] Reaction conditions: [Ni] = 4.00×10^{-5} M, 1300 equiv of Al/equiv of Ni, 50.0 mL of toluene, 0 °C, 1 atm of propylene. [b] Areas relative to an octane internal standard as determined by GLC.

Scheme 4. General Catalytic Cycle for Propylene Dimerization



intermediate,[57,58] which in this case would be (N∧N)-Ni−H$^+$. As discussed above, it is unlikely such a discrete hydride intermediate is generated; the proposed general catalytic dimerization cycle is shown in Scheme 4. Scheme 5 outlines the specific steps which lead to formation of various hexene isomers. As shown in Scheme 5, the isomers formed depend on (1) whether *n*-propyl or isopropyl group migration occurs, (2) whether migration occurs in a 1,2- or 2,1-fashion, and (3) what the direction of *β*-H elimination is when two possibilities exist (routes B and D). On the basis of the analysis of ethylene oligomerization above and the observation of branching in ethylene polymerization by similar Ni catalysts as well as recent observations concerning cationic palladium alkyl complexes,[46] it is likely that the cationic nickel propyl complexes **V** and **VI** as well as the nickel propyl propylene complexes **VII** and **VIII** partially or fully equilibrate prior to migratory insertion.

Scheme 5. Propylene Dimerization Pathways



Some isomerization of primary dimerization products takes place (see Table 3). Since 2-methyl-2-pentene is the major isomerization product and it can arise from either pathway A or D, the fraction of reaction through one or both of these pathways may be underestimated using ratios of primary products. However, since isomerization products account for only 10% of total product, qualitative conclusions can be drawn from primary product ratios. Clearly pathway B, involving 2,1-insertions of the *n*-propyl complex, is the major pathway for dimerization, accounting for 40% of primary products observed. Products from migration of an *n*-propyl group (both 2,1 and 1,2) are favored over products from migration of an isopropyl group by ca. 2:1 (paths A +

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(57) Müller, U.; Keim, W.; Krüger, C.; Betz, P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1011−1013.

(58) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Complexes*; University Science Books: Mill Valley, CA, 1987; pp 578−596.

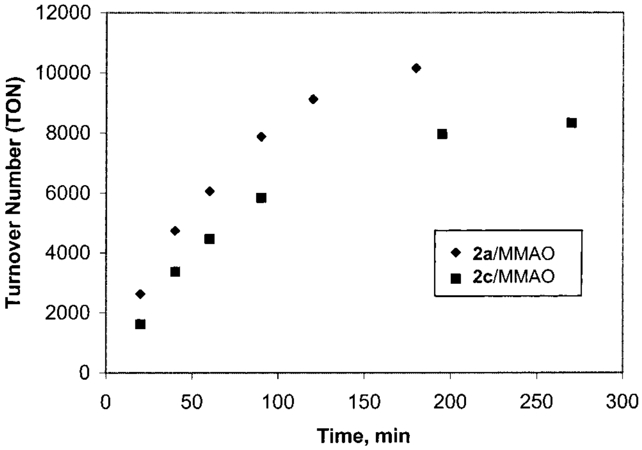

Figure 3. Propylene turnover number (TON) vs time using **2a**/MMAO and **2c**/MMAO in toluene at 0 °C.

Table 5. Dimerization of Propylene with 2a/MMAO[a]

reaction time (min)	dimer product distribn, mol %			
	n-hexenes	2-methylpentenes	2,3-dimethylbutenes	isomerizn products
20	44	47	9	12
40	45	46	9	12
60	45	46	9	12
90	46	45	9	12
120	45	46	9	12
180	45	46	9	13

[a] Reaction conditions: 2.0×10^{-6} mol of **2a**, 1300 equiv of Al/equiv of Ni, 50 mL of toluene, 1.1 atm of propylene, 0 °C.

B: paths C + D). However, since the ratios of propyl to propylene complexes (**VII**:**VIII**) undergoing insertion is not known (and they may be in equilibrium), it is not valid to conclude that the barrier to migration of the *n*-propyl group is less than that of the isopropyl group. Overall, 2,1-insertion is favored over 1,2-insertion by ca. 2:1 (paths B + D: paths A + C).

It is also instructive to examine the 2,1:1,2 insertion ratio as a function of which group, *n*-propyl or isopropyl, is migrating. Again, on the basis of ratios of primary products, the *n*-propyl group exhibits a ca. 2:1 ratio of 2,1:1,2 insertion (path B:A) while the corresponding isopropyl group ratio (path D:C) is ca. 2.5:1. Thus, 2,1-insertion is somewhat preferred for the secondary alkyl group. This preference may be somewhat greater when considering that the 2-methyl-2-pentene isomerization product, no matter which pathway it forms from, either decreases the B:A ratio or increases the D:C ratio.

The catalyst lifetimes under typical propylene dimerization conditions used to construct Table 3 were examined by analyzing aliquots of dimerization reactions catalyzed by **2a**/MMAO and **2c**/MMAO and plotting the total propylene turnover number vs time (Figure 3). Both catalysts demonstrate relatively steady activity for the first 40 min following activation, but subsequently their performance degrades. Following 2 h of reaction time, the catalysts are still functioning, but slowly. The dimer product distribution remains constant throughout the duration of the experiment, as well as the extent to which these products are isomerized (Table 5). During the early periods of the reaction the sole reaction products are dimers. At longer reaction times (e.g. after 2 h), small amounts of trimers appear, but even after 3 h they comprise less than 2% of the total product mixture. No tetramers or higher oligomers were detected by gas chromatography. Similar results were obtained from the dimerization reaction catalyzed by **2c**/MMAO.

Table 6. Dimerization of 4-Methyl-1-pentene by 2a/MMAO in Toluene

species	product distribn, mol %	
	1 h aliquot	2 h aliquot
4-methyl-1-pentene	89.6	86.9
cis-4-methyl-2-pentene	1.3	1.6
trans-4-methyl-2-pentene	1.4	1.8
2-methyl-1-pentene	1.4	1.7
2-methyl-2-pentene	1.5	1.9
dimers[a]	4.8	6.1
dimer TON (mol of dimers/mol of Ni)	205	270

[a] Includes all C_{12} alkenes.

D. Dimerization of Higher Olefins. Dimerization reactions of 1-butene and 4-methyl-1-pentene run under conditions similar to the propylene dimerization reactions were analyzed by GLC and found to proceed only very slowly as compared to propylene dimerizations. 1-Butene is dimerized by **2a**/MMAO at a rate less than 10% of that observed for propylene dimerizations run under similar reaction conditions.

The results of dimerization of 4-methyl-1-pentene by **2a**/MMAO are listed in Table 6. While small amounts of dimers are produced, this catalyst system actually isomerizes 4-methyl-1-pentene at a faster rate than it dimerizes it. Turnover frequencies are less than 5% of those measured for propylene dimerizations carried out under similar conditions. Overall, these results suggest that uptake of olefin products in ethylene oligomerizations should occur much more slowly than ethylene, and this is experimentally borne out by both the observed Schulz–Flory oligomer distributions and the lack of branched olefin products.

Conclusions

The findings that sterically unhindered (α-diimine)-nickel(II) catalysts actively oligomerize ethylene and dimerize propylene further demonstrate the versatility of this class of catalysts and illustrate their sensitivity to steric tuning. The temperature and pressure sensitivity of these catalysts in ethylene oligomerization reactions allows control of the reaction products through simple variation of these reaction conditions. Ethylene oligomer mixtures with longer average chain lengths can be produced by increasing the ethylene pressure, lowering the reaction temperature, and using Et_2AlCl as the cocatalyst, while oligomer mixtures with shorter average chain lengths can be produced by lowering the ethylene pressure, raising the reaction temperature, and using MAO or MMAO as the cocatalyst. Lowering the electron density on the metal center through addition of electron-withdrawing groups on the ligand produces more active catalysts but leads to slightly lower selectivity for α-olefins. Catalyst longevity in ethylene oligomerization reactions is dependent upon the nature and concentration of aluminum cocatalyst, and MAO-IP was found to be the best cocatalyst for generating long-lived catalysts.

These catalysts are very active propylene dimerization catalysts and demonstrate some selectivity for linear products. Maximum turnover frequencies are realized using electrophilic precatalysts activated with MMAO at temperatures near 0 °C and propylene pressures above 2 atm. Slow dimer product isomerization takes place under typical reaction conditions and can be minimized by lower temperatures and higher propylene pressures. The dimer product distribution indicates a 2:1 preference for an initial 1,2-propylene insertion (versus a 2,1-insertion). Furthermore, a 2:1 preference for the second propylene inserting in a 2,1-fashion is observed. Higher olefins such as 1-butene and 4-methyl-1-pentene are dimerized very slowly relative to propylene, which is further evidence that reincorporation of higher olefin reaction products in both ethylene oligomerization and propylene dimerization reactions is not favorable.

Experimental Section

General Methods. All manipulations of air- and/or water-sensitive compounds were performed using standard high-vacuum or Schlenk techniques. Argon was 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. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Varian XL-400 MHz or Gemini 300 MHz spectrometers. Chemical shifts are reported relative to residual $CHCl_3$ (δ 7.24 for ^{1}H), $CDCl_3$ (δ 77.00 for ^{13}C), and CCl_3F (δ 0.00 for ^{19}F). The dimer and oligomer products were analyzed on a Hewlett-Packard 5890A gas chromatograph using a Supelco Petrocol DH 50.2 capillary column (50 m, 0.20 mm i.d., 0.50 μm film thickness) and a flame ionization detector. Ethylene flow measurements were made with an Omega FMA-869 mass flowmeter and recorded with an Omega RD-853-T paperless recorder. Elemental analyses were performed by Atlantic Microlab of Norcross, GA.

Materials. Toluene, diethyl ether, pentane, and methylene chloride were purified using procedures recently reported by Pangborn et al.[59] Polymer-grade ethylene and propylene were purchased from National Specialty Gases. Propylene was passed through a Drierite gas drying jar (6.7 cm × 29 cm column) before use, while ethylene was used without further purification. We purchased 7% Al (wt %) and 6.4% Al solutions of modified methylalumoxane (MMAO) in heptane containing 23−27% isobutyl groups from Akzo Nobel. MAO-IP (13.5 wt % Al in toluene) was purchased from Akzo Nobel. Diimine ligands **1b**−**e** and corresponding nickel(II) bromide complexes **2b**−**e** were prepared according to modified literature procedures.[31,37,39,40] Acenaphthoquinone, 4-(trifluoromethyl)aniline, $(DME)NiBr_2$, MAO, Et_2AlCl, and 1-pentene were purchased from Aldrich Chemical Co. and used as received. The hexene isomer standards were purchased from Aldrich, Lancaster, and Fluka.

Synthesis of ArN═C(An)C(An)═NAr (Ar = *p*-$CF_3C_6H_4$; 1a). Acenaphthoquinone (0.514 g, 2.82 mmol) and 4-(trifluoromethyl)aniline (1.00 g, 6.20 mmol) were added to 40 mL of dry toluene in a round-bottom flask equipped with a magnetic stir bar. Camphorsulfonic acid catalyst (15 mg) was added to the reaction mixture, and a Dean−Stark trap was attached to the flask. The solution was refluxed for 5 days. Toluene was then removed on a vacuum line, leaving an orange solid. The solid was dissolved in 5 mL of $CHCl_3$, and 40 mL of pentane was then added to precipitate the diimine. The precipitate was washed with 2 × 20 mL of pentane and dried in vacuo. The product was isolated as a yellow solid (1.06 g, 80% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, 30 °C): δ 7.94 (d, J = 8.1 Hz, 2 H), 7.73 (d, J = 8.1 Hz, 4 H), 7.42 (pseudo t, 2 H), 7.21 (d, J = 8.1 Hz, 4 H), 6.84 (d, J = 7.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz, 30 °C): δ 161.3, 154.5, 142.0, 131.4, 129.6, 128.0, 127.9, 126.8 (q, $^{3}J_{C-F}$ = 3.3 Hz), 126.7 (q, $^{2}J_{C-F}$ = 33.4 Hz), 124.4 (q, $^{1}J_{C-F}$ = 271 Hz, CF_3), 124.1, 118.3; ^{19}F NMR ($CDCl_3$, 282 MHz, 20 °C) δ −62.3 (s, CF_3). Anal. Calcd for $C_{26}H_{14}F_6N_2$: C, 66.67; H, 3.01; N, 5.98. Found: C, 66.69; H, 3.08; N, 5.90.

Synthesis of (ArN═C(An)C(An)═NAr)$NiBr_2$ (Ar = *p*-$CF_3C_6H_4$; 2a). $(DME)NiBr_2$ (77 mg, 0.25 mmol) and **1a** (150 mg, 0.32 mmol) were combined in a Schlenk flask under an argon atmosphere. CH_2Cl_2 (20 mL) was added, and the reaction mixture was stirred at room temperature for 20 h. The supernatant liquid was removed, and the product washed with 3 × 10 mL of Et_2O and dried in vacuo. The product was isolated as an olive green powder (141 mg, 82% yield). MS (FAB): *m/z* [%] 610, 609, 608, 607, 606, 605 [12, 35, 32, 100, 23, 72, $M^+ - Br$], 529, 528, 527, 526 [6, 15, 13, 35, $M^+ - Br_2$], 470, 469, 468 [10, 26, 8, $M^+ - NiBr_2$], 450, 449 [17, 52, $M^+ - NiBr_2F$]. Anal. Calcd for $C_{26}H_{14}Br_2F_6N_2Ni$: C, 45.46; H, 2.05; N, 4.08. Found: C, 45.31; H, 2.70; N, 3.75.

General Procedure for Ethylene Oligomerization. A mechanically stirred 1000 mL Parr autoclave was heated overnight to 100 °C under vacuum and then cooled to 30 °C under an ethylene atmosphere. The autoclave was charged with 198 mL of toluene and MMAO. The autoclave was sealed, and ethylene was added (100 psig). The solution was stirred for 10 min, during which time the desired reaction temperature was established. The ethylene pressure was then released, and a suspension of the appropriate catalyst precursor (**2a**−**d**, 2.0 × 10^{-5} mol in 2 mL of toluene) was added to the reaction mixture via cannula. The reactor was then sealed and pressurized with ethylene to the desired reaction pressure. The reaction mixture was stirred under constant ethylene pressure for 1 h, after which time the pressure was released and the catalyst quenched with acetone and water. An aliquot of the reaction mixture was analyzed by GLC to determine the Schulz−Flory α constant. The integrated areas of the C_{12} and C_{14} oligomers were used to calculate the Schulz−Flory α constants. The GLC conditions used are as follows: injector and detector temperatures, 250 °C; oven temperature program, 100 °C/4 min, 8 °C/min ramp, 250 °C/70 min. Oligomer peaks in the C_4−C_{26} range were resolved under these analytical conditions. The solvents were removed on a rotary evaporator, and the residual toluene was removed in vacuo overnight. The mass of the remaining olefin products was obtained, and lower olefins lost during workup were calculated using the Schulz−Flory α constant and a gas chromatograph taken of the olefin products following workup. α-Olefin selectivity was determined by comparing the ratios of terminal olefin proton areas to internal olefin proton areas as measured by ^{1}H NMR spectroscopy.

Ethylene Flow Rate Measurements. A mechanically stirred 1000 mL Parr autoclave under an ethylene atmosphere was charged with 198 mL of toluene and the appropriate aluminum cocatalyst. The reactor was sealed and pressurized with ethylene to 200 psig, and the temperature was allowed to equilibrate at 35 °C. Once the system reached equilibrium, the ethylene flow baseline was established with a mass flowmeter positioned between the ethylene supply cylinder and the autoclave. A small flame-dried Schlenk tube under an argon atmosphere was charged with **2a** (1.0 × 10^{-5} mol, 6.9 mg) and 2 mL of toluene to form a precatalyst slurry. The reactor was vented, and the precatalyst slurry was transferred into the reactor via cannula. The reactor was repressurized to 200 psig with ethylene, and the temperature was maintained at 35 °C. Ethylene flow rates were recorded at 5−15 s intervals throughout the duration of the reaction.

General Procedure for Propylene Dimerization. A dry Fisher−Porter bottle was charged with a magnetic stir bar,

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

evacuated, and then filled with propylene. Toluene (47.0 mL) and MMAO (1.4 mL of 7% heptane solution) were added to the bottle via syringe. The reaction mixture was then cooled to the reaction temperature while being stirred under constant propylene pressure. A suspension of the appropriate catalyst precursor (**2a**−**d**, 2.00 × 10^{-6} mol in 2.0 mL of toluene) and 50 μL of octane (internal standard) were transferred via cannula to the reaction vessel. The bottle was then sealed and pressurized with propylene. After a 30 min reaction period, the reactor was depressurized, and an aliquot of the reaction mixture was removed for GLC analysis. The GLC conditions used: injector temperature. 220 °C; detector temperature, 250 °C; oven temperature program, 30 °C/18 min, 20 °C/min ramp, 150 °C/25 min.

Analysis of Propylene Dimers. Standard solutions of the propylene dimers and octane were prepared by adding 2.5, 5.0, 10.0, and 15.0 μL of authentic samples of each compound to toluene in 10.0 mL volumetric flasks. The solutions were diluted to 10.0 mL with toluene, and GLC calibration curves were obtained. Aliquots of the dimerization reaction mixtures (*ca*. 5 mL) were removed via cannula and added to 10.0 mL volumetric flasks containing about 4 mL of acetone. The aliquots were warmed to 20 °C, diluted to volume with acetone, and injected into the gas chromatograph. Each dimer was qualitatively identified by retention time. Retention times for the dimers under the analytical conditions used are as follows: 4-methyl-1-pentene, 10.92 min; 2,3-dimethyl-1-butene, 11.55 min; *cis*-4-methyl-2-pentene, 11.65 min; *trans*-4-methyl-2-pentene, 11.85 min; 2-methyl-1-pentene, 13.19 min; 1-hexene, 13.28 min; *trans*-3-hexene, 14.48 min; *cis*-3-hexene, 14.57 min; *trans*-2-hexene, 14.73 min; 2-methyl-2-pentene, 14.96 min; *cis*-2-pentene, 15.66 min; 2,3-dimethyl-2-butene, 17.59 min. The dimers were quantified by first determining the volume of the aliquot withdrawn via comparison of the octane internal standard area with an octane calibration curve and then using the GLC areas of each propylene dimer versus their respective standard calibration curves to determine the mass of each dimer present in the reaction mixture.

1-Pentene Isomerization Control Experiment. The general procedure described for propylene dimerization was followed (*vide supra*). A slurry of precatalyst **2a** (1.37 mg, 2.00 × 10^{-6} mol) in 2.0 mL of toluene was added to MMAO (1.5 mL of 6.4% heptane solution, 1300 equiv of Al/equiv of Ni) in 46.5 mL of toluene containing 50 μL of 1-pentene and 50 μL of octane at 0 °C. The propylene pressure was maintained at 1 atm throughout the duration of the experiment. Aliquots (ca. 5 mL) of the reaction mixture were removed at 5 min, 1 h, and 2 h after catalyst activation and analyzed by GLC. The areas of 1-pentene, *cis*-2-pentene, and *trans*-2-pentene relative to an octane internal standard were determined for each aliquot.

Propylene Dimerization Longevity Experiments. The general procedure described for propylene dimerization was followed (*vide supra*). A slurry of precatalyst **2a** (1.37 mg, 2.00 × 10^{-6} mol) or **2c** (1.16 mg, 2.00 × 10^{-6} mol) in 2.0 mL of toluene was added to MMAO (1.4 mL of 7% solution, 1300 equiv of Al/equiv of Ni) in 46.6 mL of toluene containing 50 μL of octane at 0 °C. The propylene pressure was maintained at 1.1 atm throughout the duration of the experiment. Aliquots (ca. 4 mL) of the reaction mixture were removed via cannula and quantified by GLC (*vide supra*). The amounts of catalyst, solvent, and dimer products removed with each aliquot were determined using the octane internal standard and utilized in subsequent turnover number calculations.

Dimerization of 1-Butene. Precatalyst **2a** (5.0 × 10^{-6} mol, 3.4 mg) and 50 mL of toluene were combined in a 100 mL Schlenk flask equipped with a magnetic stir bar. 1-Butene was purged through the solution for 10 min, and then 1.2 mL of MMAO (7% in heptane) was added via syringe. The reaction was allowed to proceed at 25 °C for 75 min under 1 atm of 1-butene pressure. Aliquots were removed at 10 and 75 min, quenched with acetone, and injected into the GLC (60 °C isothermal). A mixture of butene dimers was observed. Comparison of total dimer GLC areas with propylene dimer standards shows the turnover frequencies for 1-butene dimerization are less than 10% of those observed for analogous propylene dimerization reactions.

Dimerization of 4-Methyl-1-Pentene. Dry, degassed toluene (48 mL) was added to a dry, Ar-filled 100 mL Schlenk flask equipped with a magnetic stir bar. 4-Methyl-1-pentene (ca. 1 mL) was added to the reaction mixture via syringe, followed by MMAO (1.5 mL of a 6.42% solution). Precatalyst **2a** (2.00 × 10^{-6} mol, 1.37 mg), octane (52.5 μL, GLC internal standard) and 2 mL of toluene were added to a flame-dried Schlenk tube. The precatalyst slurry was transferred into the reaction flask via cannula. The reaction was allowed to proceed at 25 °C under a static Ar atmosphere for 2 h. Aliquots of the reaction mixture were removed after 1 and 2 h, quenched in acetone, and analyzed by GLC using the procedure described above for quantitative analysis of propylene dimers. The product distributions are listed in Table 6. Turnover numbers based on dimer masses calculated using the 4-methyl-1-pentene GLC calibration curve are 205 mol of dimers/mol of Ni (1 h aliquot) and 270 mol of dimers/mol of Ni (2 h aliquot).

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