# *Articles*

# Tridentate Cobalt Catalysts for Linear Dimerization and Isomerization of α-Olefins

Brooke L. Small*

*Chevron Phillips Chemical Company LP, 1862 Kingwood Drive, Kingwood, Texas 77339*

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Upon activation with modified methylalumoxane (MMAO), tridentate pyridine bisimine cobalt catalysts dimerize α-olefins with lower productivity than analagous iron systems, as indicated by comparing the batch dimerization of 1-butene (TON ~42 000 for Co, ~147 000 for Fe). The cobalt-produced dimers are extremely linear (>97%) and contain only traces of trimeric species. The cobalt catalysts also have a tendency to isomerize α-olefins, as evidenced by the approximately equal levels of dimerization and isomerization achieved when 1-butene is dimerized. When the cocatalyst is changed to diethylaluminum chloride, isomerization occurs exclusively to give *cis*- and *trans*-2-olefins selectively. To mitigate the effects of feed isomerization, dimerization of propylene was also studied. GC analysis of the products reveals a stepwise oligomerization process that makes linear hexenes, nonenes, and dodecenes, with the hexenes comprising up to 70% of the product mix. The hexenes are over 99% linear and may contain over 50% 1-hexene. Catalyst productivity is high, with turnover numbers exceeding 200 000 mol propylene/mol Co (17 000 g oligomers/g Co complex).

## Introduction

The dimerization of olefins by transition metal complexes represents an important class of industrially relevant chemistry.[1] For example, ethylene dimerization to 1-butene can provide a source of comonomer in the production of polyethylene,[2] and olefins such as propylene and butene are dimerized to give $C_6$–$C_8$ materials that serve as feedstocks for gasoline blending or alcohol production.[3] While most dimerization catalysts produce branched dimers from propylene and higher olefins, we recently reported a family of iron-based catalysts that make predominantly linear dimers (up to 80% linearity).[4] Due to a unique mechanism of dimerization in which the regiochemistry of olefin insertion changes from 1,2 to 2,1 between the first and second steps,[5] the major product is the head-to-head dimer (Scheme 1).

The major byproduct in the reaction is the methyl-branched dimer, which results from two successive 2,1 insertions followed by chain termination. In addition, approximately 15% of the product is a lightly branched olefin trimer, which possesses an average of ≥1.2 branches per molecule. The final product in the reaction is the undimerized olefin substrate, which often contains several percent of isomerized material due to chain transfer following an initial 2,1 insertion (Scheme 2).

In an attempt to expand this dimerization chemistry to other transition metals, several tridentate cobalt complexes were synthesized and tested for their dimerization ability.[6] Remarkably, some of these cobalt catalysts are much more selective for producing linear dimers than their iron analogues, while other systems are highly selective for isomerizing the starting material. Herein are reported the details of this cobalt catalyst study.

## Results and Discussion

Cobalt complexes **1**–**4**, shown in Figure 1, were synthesized by reported methods and tested for their ability to dimerize α-olefins.[7–9] In efforts to compare

* Corresponding author.

(1) (a) Chauvin, Y.; Olivier, H. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W., Eds.; VCH: New York, 1996; Vol. 1, pp 258–268. (b) Skupinska, J. *Chem. Rev.* **1991**, *91*, 613. (c) Parshall, G. W.; Ittel, S. D. In *Homogeneous Catalysis, The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes,* 2nd ed.; John Wiley & Sons: New York, 1992; pp 72–85. (d) Bhaduri, S.; Mukesh, D. In *Homogeneous Catalysis, Mechanisms and Industrial Applications*; John Wiley & Sons: New York, 2000; pp 142–147.

(2) Al-Jarallah, A. M.; Anabtawi, J. A.; Siddiqui, M. A. B.; Aitani, A. M.; Al-Sa'doun, A. W. *Catal. Today* **1992**, *14* (1).

(3) (a) Olivier-Bourbigou, H.; Chodorge, J.-A.; Travers, P. *Pet. Technol. Q.* **1999**, *Autumn*, 141. (b) Chauvin, Y.; Gaillard, J. F.; Quang, D. V.; Andrews, J. W. *Chem. Ind.* **1974**, 375. (c) Commereuc, D.; Chauvin, Y.; Gaillard, J.; Léonard, J.; Andrews, J. W. *Hydrocarbon Process.* **1984**, 118.

(4) (a) Small, B. L.; Marcucci, A. J. *Organometallics* **2001**, *20*, 5738. (b) Small, B. L.; Baralt, E. J.; Marcucci, A. J. (Chevron Phillips) U.S. Patent 6291733, 2001.

(5) (a) Small, B. L.; Brookhart, M. *Macromolecules* **1999**, *32*, 2120. (b) Pellecchia, C.; Mazzeo, M.; Pappalardo, D. *Macromol. Rapid Commun.* **1998**, *19*, 651.

(6) Cobalt complexes containing pyrrole ligands have previously been reported for the dimerization of ethylene to high purity 1-butene: Wu, A. U.S. Pat. 5414178 (Phillips Petroleum), 1995.

(7) For specific ligand syntheses, see the following references: (a) Small, B. L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 7143. (b) Alyea, E. C.; Merrell, P. H. *Synth. React. Inorg. Metal-Org. Chem.* **1974**, *4* (6), 535.

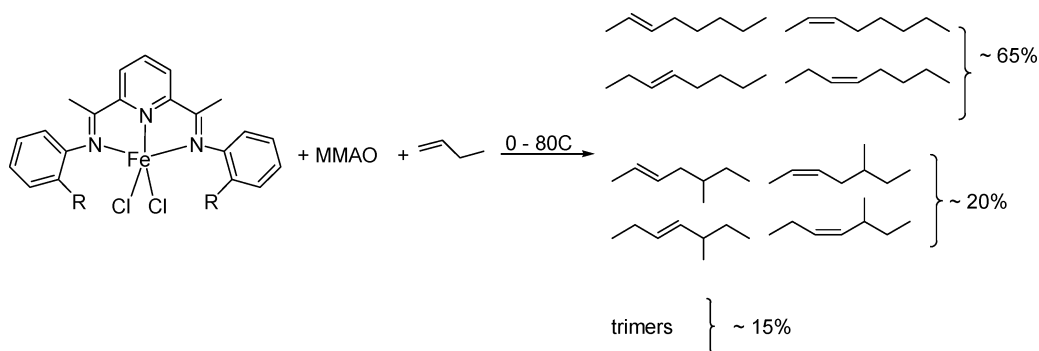**Scheme 1.   Dimerization of 1-Butene Catalyzed by Tridentate Iron Catalysts**



**Table 1.  Dimerization of 1-Butene Using MMAO-Activated Cobalt Complexes 2−4**

| entry | cat./mass (mg) | Al:Co ratio | $C_4$ mass (g) | $T$ (°C) | rxn length (h) | prod. mass (g) | % conversion[a] | productivity (g dimer/g Co complex) | % dimer | % linear dimer | D/I ratio[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **2**/25 | 500 | 250 | 30 | 3 | 97.7 | 39.1 | 3910 | 99 | 97 | 0.70 |
| 2 | **3**/25 | 500 | 250 | 30 | 3 | 51.4 | 20.6 | 2060 | 99 | 98 | 0.71 |
| 3 | **3**/82 | 200 | 1080 | 30 | 5 | 340 | 31.5 | 4150 | 99 | 98 | 0.72 |
| 4 | **4**/25 | 500 | 250 | 30 | 3 | 11.7 | 4.7 | 470 | 97 | 98 | 0.47 |
| 5 | **2′**/10[c] | 500 | 250 | 30 | 3 | 153 | 61.2 | 15 300 | 82 | 70 | >20 |

[a] Does not include isomerized butene. [b] D/I ratio = mass ratio of (dimerized + trimerized butene)/isomerized butene. [c] **2′** = Fe analogue of Co complex **2**.

**Scheme 2.   Formation of Branched Dimers and Isomerized Starting Materials**
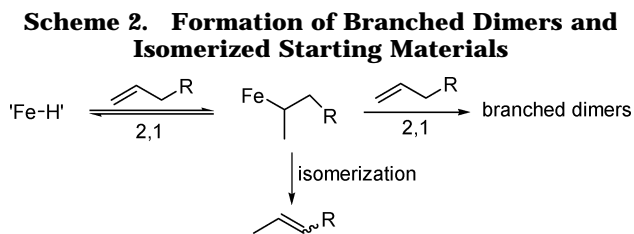


these systems to our earlier results using iron, 1-butene was dimerized in liquid phase to assess the catalyst activity. The results of these reactions are reported in Table 1. Unlike the analogous tridentate iron systems, these cobalt catalysts produce extremely low levels of methyl-branched heptenes in the octene products, resulting in 97%+ linearity in the dimers (entries 1−4). Figure 2 shows the analysis of the $C_8$ portion of entry 2 by GC/MS. Also, the cobalt systems make only traces of butene trimer, in comparison to the iron systems, which produce about 15% trimer (entry 5). Comparing the catalyst activities, the cobalt systems are slower than iron, and the overall catalyst productivity of the iron system is several times higher than cobalt under similar operating conditions (Fe ~15 300 g product/g Fe complex; Co ~4150 g product/g Co complex). Both systems may be activated with relatively low amounts of alumoxane cocatalysts (<200:1 Al:cat molar ratios, entry 3).[10]
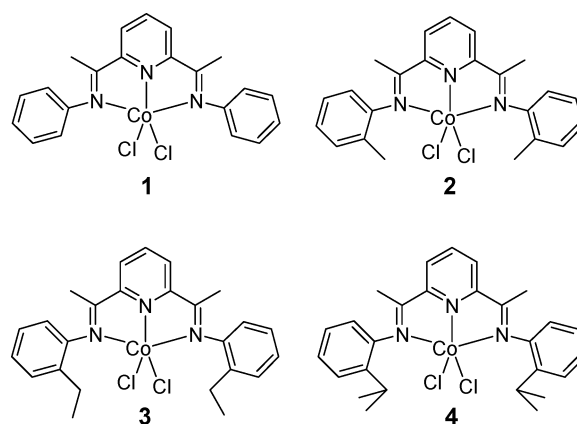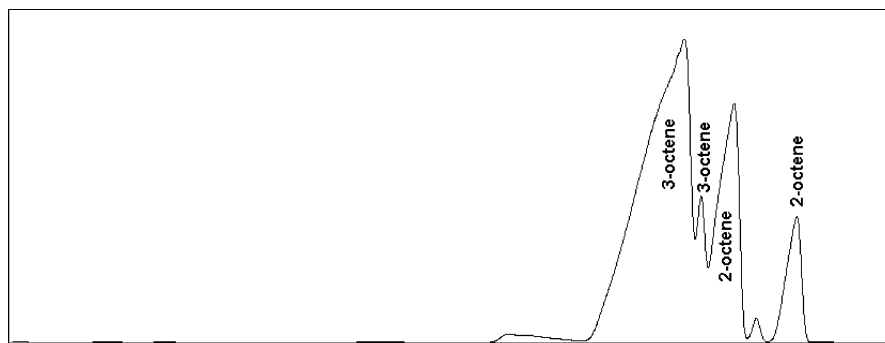


**Figure 1.**  Cobalt complexes **1**−**4**.

To better understand the remarkable selectivity of the cobalt catalysts, it was useful to examine the undimerized butene. With the iron-based catalysts, the α-olefin feed was only lightly isomerized (entry 5). With cobalt, however, complexes **1**−**4** tend to isomerize the substrate heavily, resulting in the production of substantial quantities of 2-butene in the undimerized olefin. As noted earlier, isomerization occurs when an initial 2,1 (secondary) insertion of olefin is followed by β-elimination with opposite regiochemistry. For iron, initial 2,1 insertions tend to produce branched dimers, indicating that propagation is preferred; cobalt, on the other hand, undergoes chain transfer following a 2,1 insertion, resulting in both highly linear dimers and high amounts of isomerization in the feed. These observations show that cobalt is likely not more regioselective than iron

(8) For specific Co complex syntheses, see the following references: (a) Edwards, D. A.; Edwards, S. D.; Martin, W. R.; Pringle, T. J. *Polyhedron* **1992**, *11* (13), 1569. (b) Britovsek, G. J. P.; Mastroianni, S.; Solan, G. A.; Baugh, S. P. D.; Redshaw, C.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; Elsegood, M. R. J. *Chem. Eur. J.* **2000**, *6* (12), 2221.

(9) For general synthetic details for preparing pyridinebisimine cobalt complexes, see, for example, the following references: (a) Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049. (b) Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 849. (c) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (d) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428.

(10) A ratio of 500:1 Al:Co was chosen to ensure rapid activation and the scavenging of residual moisture in the reactions. However, our studies have shown that this ratio can be greatly reduced when the scale of the reaction is increased. Entry 3 illustrates this trend, which was also observed for the Fe-based catalysts (ref 4a). Table 3, in which polymer grade propylene (<1 ppm $H_2O$) was used, demonstrates that low Al:Co ratios can be achieved when the olefin is substantially free of moisture.
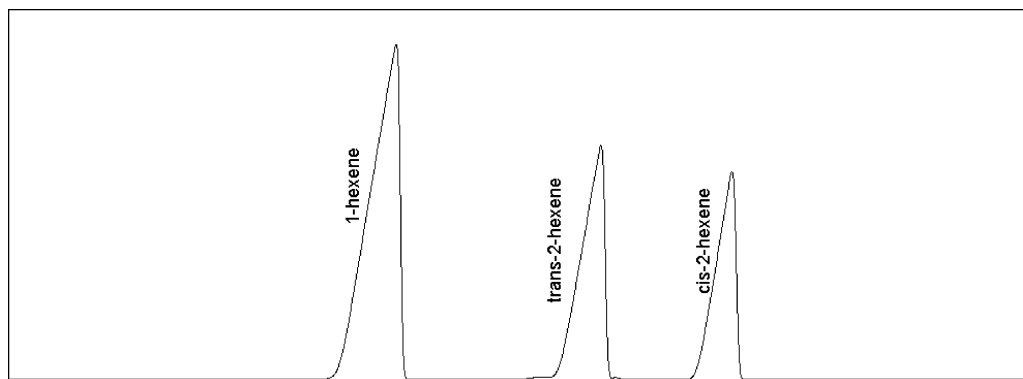
**Figure 2.** GC trace of 1-butene dimers made by MMAO-activated cobalt catalyst **3** (Table 1, entry 2).

**Table 2. Oligomerization of Propylene Using MMAO-Activated Cobalt Complexes 2−4$^a$**

| entry | cat./ mass (mg) | Al:Co ratio | $C_3$ mass (g) | prod. mass (g) | % Conv. | productivity (g olig./g Co complex) | mass $C_6$ (g) | % linear$^b$ | % 1-hexene$^c$ | mass $C_9$ (g)$^d$ | mass $C_{12+}$ (g) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **2**/20 | 100 | 400 | 304 | 76 | 15 200 | 177 | 99.0 | 10 | 87 | 40 |
| 2 | **3**/20 | 100 | 400 | 231 | 58 | 11 600 | 105 | 99.7 | 14 | 72 | 54 |
| 3 | **4**/20 | 100 | 400 | 187 | 47 | 9400 | 130 | 99.9 | 59 | 47 | 11 |
| 4 | **2**/20 | 150 | 400 | 342 | 86 | 17 100 | 200 | 99.0 | 8 | 97 | 45 |
| 5 | **3**/20 | 150 | 400 | 312 | 78 | 15 600 | 142 | 99.7 | 22 | 101 | 69 |
| 6 | **4**/20 | 150 | 400 | 147 | 37 | 7400 | 112 | 99.8 | 57 | 28 | 6 |

$^a$ Reaction conditions: Each reaction was run for 20 h at 30 °C. $^b$ % linear = % linearity of the $C_6$ fraction. $^c$ % 1-hexene = % 1-hexene in the $C_6$ fraction. $^d$ All of the nonene products contained significant quantities of 1-nonenes. Entry 6, for example, contained 34% 1-nonene in the $C_9$ fraction.



**Figure 3.** GC trace of propylene dimers made by MMAO-activated cobalt complex **4** (57% 1-hexene, Table 2, entry 6).

at the point of initial insertion, but rather that the cobalt systems promote propagation (dimerization) only when a cobalt-*n*-alkyl species is present. This implies that if the isomerization side reaction could be suppressed, it would likely be achieved at the expense of dimer linearity, since initial 2,1 insertions would lead to branched dimer formation.

To remove feed isomerization as a possibility, a study of propylene dimerization was undertaken, the results of which are summarized in Table 2. Propylene oligomerization with tridentate cobalt catalysts has been reported by Bennett;[11] however, the catalysts used in this study are less sterically bulky than those described in the earlier report. The experiments in Table 2 employ cobalt catalysts bearing a single *ortho* substituent on each aryl ring, and the results illustrate several unique trends. First, the catalysts are highly active, with catalyst productivities exceeding 17 000 g product/g Co complex (entry 4). Second, not only do the catalysts produce extremely linear dimers (Figure 3), but the trimer products are also highly linear (Figure 4). GC/

MS analysis of the $C_9$ fraction made by catalyst **4** revealed 95% linearity in the nonenes, a clear indicator that the $C_9$ and $C_{12}$ byproducts are formed by a step growth dimerization process (chain transfer following each insertion). As further evidence for a step growth process, analysis of the linear nonenes by GC/MS also did not reveal any 3-nonenes, which agrees with the proposed catalytic cycle shown in Scheme 3. Furthermore, the nonenes made by catalyst **4** were found to contain over 30% 1-nonene (Table 2, entry 6), a result of codimerization of 1-hexene and propylene, with propylene involved in the second insertion step.

As shown in Scheme 3, perhaps the most interesting feature of these catalysts is their ability to make 1-hexene from propylene. Under the conditions employed in this report, it was possible to isolate a propylene-based oligomer in which 70% of the products were *n*-hexenes with over 99.8% linearity. Of these hexenes, 59% were the 1-hexene isomer, representing an overall product distribution that contained 41% 1-hexene (catalyst **4**, entry 3). Both the linearity of the dimerization process and the selectivity for 1-hexene

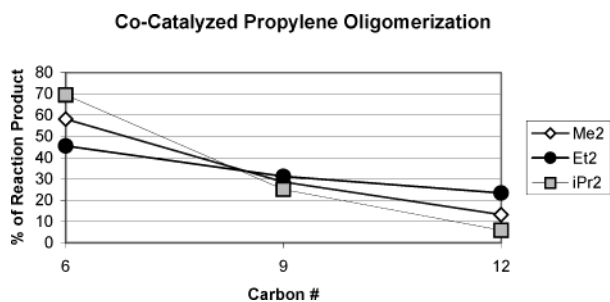(11) Bennett, A. M. A. (DuPont) U.S. Patent 6063881, 2000.
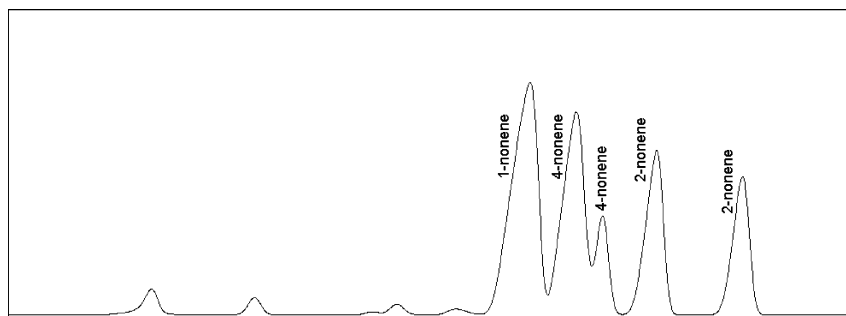
**Figure 4.** GC trace of propylene trimers made by MMAO-activated cobalt complex **4** (34% 1-nonene, Table 2, entry 3).

**Scheme 3. Proposed Mechanism for Cocatalyzed Propylene Oligomerization**[a]
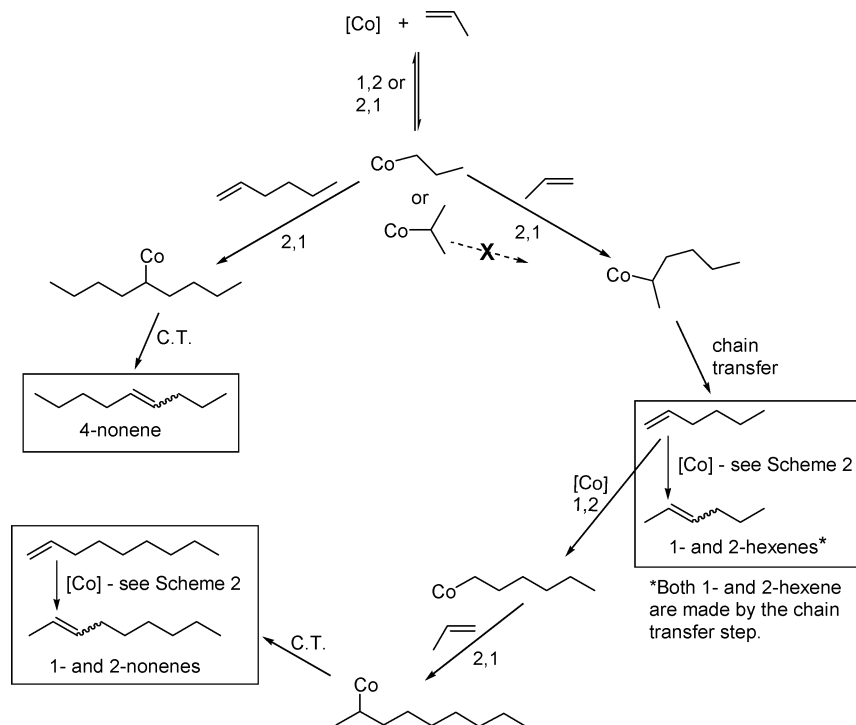


[a] Dodecene formation is omitted for clarity; [Co] = unobserved cobalt initiating species.



**Figure 5.** Product distribution by carbon number for catalysts **2**–**4**, entries 1–3 in Table 2 ($C_{12}$ refers to $C_{12+}$).

are, to our knowledge, unprecedented for propylene dimerization.

Figure 5 shows the product distribution by carbon number for catalysts **2**–**4**, taken from entries 1–3 of Table 2. Interestingly, catalyst **4**, the most sterically bulky system, produces the largest percentage of hexenes, which is counterintuitive when one considers the previous reports that have directly correlated product molecular weight to increasing ligand sterics.[7a,8b,9] However, because the propylene oligomerization proceeds via

a step growth rather than a chain growth mechanism, the inverse trend may be rationalized by further inspection of Scheme 3. Further step growth following a dimerization reaction requires an α-olefin such as 1-hexene, but 1-hexene's increased size relative to propylene promotes propylene uptake in the successive catalytic steps. Even though complex **4** exhibits a high selectivity for producing 1-hexene, this 1-hexene is relatively inert toward further dimerization steps. As also seen in Figure 5, this trend of hexene percentage in the total product does not remain true over the series of catalysts **2**–**4** (Me → Et → *i*Pr). While complex **4** makes the most hexenes, methyl-substituted **2** makes the second highest amount and ethyl-substituted **3** produces the lowest percentage of hexenes. This anomaly in the trend is likely due to catalyst **3** (Et) having a higher selectivity for making 1-hexene than catalyst **2** (Me) and by catalyst **3**'s ability to incorporate 1-hexene into nonenes and dodecenes more readily than catalyst **4**. These observations readily illustrate that the product composition in these types of step growth reactions will be highly dependent on the interplay of factors such as the selectivity toward 1-hexene, reaction length (residence time), and α-olefin concentrations.

**Table 3.  Comparison of Nonene and Dodecene Linearity of Oligomers Made by Catalysts 2−4**

| catalyst | $C_6$ linearity (%) | $C_9$ linearity (%) | $C_{12}$ linearity (%) | $C_{15}$ linearity (%) |
|---|---|---|---|---|
| 2/MMAO | 99.0 | 96.0 | 94.5 | 93.5 |
| 3/MMAO | 99.7 | 94.9 | 93.5 | 91.6 |
| 4/MMAO | 99.9 | 94.8 | 87.2 | 75.9 |

**Table 4.  Isomerization of 1-Hexene Using Cobalt Complexes 1 and 2[a]**

| cat./mass (mg) | cocat. | Al:Co ratio | olefin/amt (mL) | T (°C) | rxn length (h) | product distribution (% each isomer) |
|---|---|---|---|---|---|---|
| 1/10 | MMAO | 115 | 1-hexene/50 | 35 | 2 | 1.9 1-hexene<br>62.4 t-2-hexene<br>34.2 c-2-hexene<br>1.0 other hexenes<br>0.6 dimer |
| 1/28 | MMAO | 60 | 1-hexene/50 | 5 | 1 | 1.1 1-hexene<br>77.5 t-2-hexene<br>19.9 c-2-hexene<br>0.9 other hexenes<br>0.5 dimer |
| 1/10 | DEAC | 40 | 1-hexene/50 | 25 | 18 | 1.0 1-hexene<br>62.9 t-2-hexene<br>15.4 c-2-hexene<br>20.5 3-hexenes |
| 2/27 | DEAC | 40 | 1-hexene/100 | 25 | 72 | 1.0 1-hexene<br>61.2 t-2-hexene<br>15.6 c-2-hexene<br>22.0 3-hexenes<br>0.1 dimer |

[a] The effect of varying the Al:Co ratio with DEAC-activated catalysts was not investigated and would not be expected to significantly change the product distribution.

Another interesting trend was discovered upon examining the linearity of the propylene oligomers. To analyze these oligomers, they were first hydrogenated using 10% Pd/C and 1 atm of hydrogen pressure (see Experimental Section). Catalyst **4**, not surprisingly, makes the most linear hexene products because its steric bulk promotes higher regioregularity.[4] However, catalyst **4** produces the *least* linear nonenes, dodecenes, and pentadecenes (Table 3). This increased branching in the higher carbon numbers is attributable to the competing chain growth mechanism, which becomes more prevalent with increasing ligand sterics. Catalysts **2** and **3** undergo less of this chain growth propagation, thereby explaining the higher linearity of their higher carbon number products.

In our attempts to use other activating cocatalysts with these cobalt complexes, it was discovered that the ratio of dimerization to isomerization varies dramatically depending on the activator used. For example, when complexes **2−4** are activated with MMAO, dimerization and isomerization of the feed are competitive. When diethylaluminum chloride (DEAC) is used, isomerization occurs almost exclusively, resulting in the selective isomerization of 1-olefins to 2-olefins. These data are reported in Table 4. Rather than producing a thermodynamic distribution of internal olefin isomers from the α-olefin feed, the catalysts typically move the double bond only one position. After extended reaction times (of 10 days), the distribution is closer to thermodynamic, but the predominant olefin isomer remains the 2-olefin. When complex **1**, which bears no *ortho* alkyl groups on the aryl rings, is used as the precatalyst, selective isomerization occurs regardless of whether MMAO or DEAC is employed as the activator. Table 4

provides more details on isomerization reactions using 1-hexene as substrate; other α-olefins may also be used.

## Conclusion

The dimerization reactions reported herein represent the most selective linear dimerization technology known. 1-Butene dimerization catalyzed by tridentate cobalt complexes produces over 97% linear dimer, but the overall catalyst activity is lower than the previously reported iron systems. The butene dimers made by cobalt are highly linear because chain transfer is fast relative to chain propagation following an initial 2,1 insertion, which leads to a competing isomerization reaction that rivals the rate of dimerization. Because propylene cannot be isomerized to a somewhat inert internal olefin, it undergoes dimerization to make up to 99.9% linear hexenes, which may include over 40% 1-hexene in the final isolated product. The 1-hexene can also be isomerized or dimerized during the course of the reaction to form nonenes, dodecenes, and even small amounts of higher olefins. Due to the remarkable step growth oligomerization reaction, the nonenes may be over 95% linear, and they may contain over 30% 1-nonene. Because the reaction is a step growth rather than a chain growth process, the concentrations of the various products depend greatly on the interaction of many factors, some of which include the relative rates of dimerization and isomerization, the catalyst selectivity for making α-olefins or internal olefins during the chain transfer step, the overall level of conversion, and the actual catalyst structure used. Future studies will be directed toward understanding the interaction of these various factors, with a view of optimizing the process operating conditions toward the production of specific products.

## Experimental Section

**Materials.** Cobalt(II) chloride hexahydrate, 2,6-diacetylpyridine, diethylaluminum chloride, 10% Pd/C, and all aniline derivatives were purchased from Aldrich and used without further purification. Polymer grade propylene in cylinders with dip tubes for transfer of liquefied gas was purchased from Matheson Gas Products, Inc. CPChem's commercial grade of 1-butene was used without purification. CPChem's 1-hexene was degassed and dried over 3 Å molecular sieves prior to use. MMAO 3A was purchased from Akzo Nobel.

**Synthesis of Precatalyst Complexes 1−4.** Precatalyst complexes **1−4** were synthesized according to literature methods, as were the ligands used to make the complexes.[7−9] In general, the ligands were prepared by dissolving 2,6-diacetylpyridine and a slight excess (>2 equiv) of the appropriate aniline in methanol, heating the solution for 1 day under inert atmosphere with a catalytic amount of acetic acid, and recrystallizing the isolated solid from ethanol. The cobalt complexes were prepared by stirring a slight excess of the tridentate ligand with cobalt(II) chloride hexahydrate in THF for at least 1 day, then adding pentane to the solution and removing the precatalyst complexes by filtration. The complexes were all isolated in near-quantitative yield. Elemental analyses for complexes **1−4** were carried out to determine the amount of THF in the isolated precatalysts.[12] The solids were heated under vacuum at 40 °C prior to analysis. Complexes

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(12) Complex **1** has been previously reported (ref 8a), but was prepared using ethanol instead of THF as solvent.

**1**−**3** tested positive for an equivalent of THF, but complex **4** contained only trace amounts. Elemental analyses are reported as follows.

**2,6-Bis[1-(phenylimino)ethyl]pyridinecobalt(II) chloride·THF (1).** Anal. Calcd for $C_{25}H_{27}N_3Cl_2OCo$: C, 58.27; H, 5.28; N, 8.15; O, 3.10. Found: C, 57.90; H, 5.00; N, 8.50; O, 2.71.

**2,6-Bis[1-(2-methylphenylimino)ethyl]pyridinecobalt-(II) chloride·THF (2).** Anal. Calcd for $C_{27}H_{31}N_3Cl_2OCo$: C, 59.68; H, 5.75; N, 7.73; O, 2.94. Found: C, 59.32; H, 5.57; N, 8.22; O, 2.33.

**2,6-Bis[1-(2-ethylphenylimino)ethyl]pyridinecobalt-(II) chloride·THF (3).** Anal. Calcd for $C_{29}H_{35}N_3Cl_2OCo$: C, 60.95; H, 6.17; N, 7.35; O, 2.80. Found: C, 60.02; H, 5.80; N, 8.06; O, 2.37.

**2,6-Bis[1-(2-isopropylphenylimino)ethyl]pyridinecobalt-(II) chloride (4).** Anal. Calcd for $C_{25}H_{27}N_3Cl_2Co$: C, 61.49; H, 5.92; N, 7.97; O, 0.00. Found: C, 60.91; H, 5.89; N, 7.43; O, 0.16.

**Procedure for Dimerization of Liquefied Gases.** Under inert conditions, the appropriate cobalt complex was weighed out and added to an NMR tube. A small amount of methylene chloride was added to solublize the complex, and the tube was sealed. The sealed tube was then tied, using copper wire, to the internal cooling coils of a clean, dry Zipperclave reactor. The reactor was evacuated and then placed under static vacuum. A glass charger was then used to transfer the cocatalyst to the reactor, and the reactor was back-filled with argon. The liquefied gas cylinder was pressurized with a head pressure of argon and placed on a scale with ±5 g accuracy. Flexible hose was used to connect the gas cylinder to the reactor, and the desired amount of olefin was delivered to the reactor using the head pressure of the cylinder. The reactor was pressurized further with argon to ensure that the olefin remained in the liquid phase. Stirring was begun resulting in breakage of the NMR tube and activation of the catalyst. Reactor temperatures were easily maintained by internal cooling.

**Procedure for Dimerization/Isomerization of Liquid Olefins.** Under inert conditions, the appropriate cobalt precatalyst was added to a dry flask with a stirbar. The α-olefin was then added, and rapid stirring was begun to slurry the complex. The flask was placed under a slight argon purge, and the cocatalyst was added via syringe. Temperatures were maintained by use of a water cooling bath.

**Product Analysis.** After slowly adding water to deactivate the catalyst, tridecane was added as an internal standard. Hydrogenation of olefinic products was achieved using a 10% Pd/C catalyst with 1 atm of hydrogen gas slowly bubbling through the reaction suspension. Total conversion to saturated species was accomplished over several hours using 100 mg of the catalyst and 5 mL of the olefin mixture dissolved in tridecane. A Hewlett-Packard 6890 Series GC System with an HP-5 50m column with a 0.2 mm inner diameter was used for product characterization. Agilent ChemStation from Agilent Technologies was used to analyze the collected data. GC/MS data were obtained using an Agilent 5973 benchtop mass spectrometer using electron impact ionization interfaced to an HP 6890 gas chromatograph. The GC column was a J&W Scientific DB-5MS, 60 m × 0.25 mm i.d.

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